

## 101- chem GENERAL CHEMISTRY-1

**First Mid Term  
(15 marks)**

**Second Mid Term  
(15 marks)**

**Lab  
(30 marks)**

**Mid term  
(30 marks)**

**Final  
(100 marks)**

**Course# and Name: Chem-101, General chemistry-I**

**Semester credit hours: 4.0 credit. Second Term 1435-1436**

**Total Contact Hours: 39 hr. theory (Sun,Tue, Thurs 9-10)  
+ 24 hr. lab**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

---

---

---

---

---

---

---

---

## 101-Chem

**Instructor: Dr. W.Z. Al- Kayali**

**Office location: Blg. 5, T floor, Room No. 242**

**Office hours: Sun, Thurs 8:30-9:00 and 10-11**

**Mon 8:30-10, Tues 8:30-9:00**

**Email address: [wwaed1956@yahoo.com](mailto:wwaed1956@yahoo.com)**

**Total Contact Hours: 14 weeks x 3 hrs Theory**

**(Sun, Tues, Thurs 9-10)**

**14x 2 hrs Lab (Mon 10-12)**

**Mid Term Exam: (First mid-term 19/5 (12-1))**

**(Second mid-term 25/6 (12-1))**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

---

---

---

---

---

---

---

---

## General Chemistry-1

**Book: Chemistry: The Molecular Nature of Matter, 6E  
Jespersen/Brady/Hyslop**

Chapter	Subject
1	Chapter 1: The Mole and Stoichiometry (7 hrs)
2	Chapter 2: Properties of Gases (6 hrs)
3	Chapter 3: Energy and Thermodynamics (7 hrs)
4	Chapter 4: Chemical Kinetics (4 hrs)
5	Chapter 5: Properties of Solutions (5 hrs)
6	Chapter 6: Chemical Equilibrium (7 hrs)
7	Chapter 7: Acids and Bases (3 hrs)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

3

---

---

---

---

---

---

---

---

# Chapter 1

## The Mole and Stoichiometry

### Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

## International System of Units (SI)

- Standard system of units
- Metric
  - Seven Base Units

Table 2.1 The SI Base Units

Measurement	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

5

---

---

---

---

---

---

---

## Your Turn!

The SI unit of **length** is the

- A. millimeter
- B. meter
- C. yard
- D. centimeter
- E. foot

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

6

---

---

---

---

---

---

---

## Decimal Multipliers

Table 2.4 SI Prefixes—Their meanings and values<sup>a</sup>

Prefix	Meaning	Symbol	Prefix Value <sup>b</sup> (numerical)	Prefix Value <sup>b</sup> (power of ten)
exa		E		$10^{18}$
peta		P		$10^{15}$
tera		T		$10^{12}$
<b>giga</b>	<b>billions of</b>	<b>G</b>	<b>1000000000</b>	<b><math>10^9</math></b>
<b>mega</b>	<b>millions of</b>	<b>M</b>	<b>1000000</b>	<b><math>10^6</math></b>
<b>kilo</b>	<b>thousands of</b>	<b>k</b>	<b>1000</b>	<b><math>10^3</math></b>
hecto		h		$10^2$
deca		da		$10^1$
deci	tenths of	d	0.1	$10^{-1}$
centi	hundredths of	c	0.01	$10^{-2}$
milli	thousandths of	m	0.001	$10^{-3}$
micro	millionths of	$\mu$	0.000001	$10^{-6}$
nano	billionths of	n	0.000000001	$10^{-9}$
pico	trillionths of	p	0.000000000001	$10^{-12}$
femto		f		$10^{-15}$
atto		a		$10^{-18}$

<sup>a</sup>Prefixes in bold type are used most often.  
<sup>b</sup>Numbers in these columns can be interchanged with the corresponding prefix.

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

7

## Using Decimal Multipliers

- Use prefixes on SI base units when number is too large or too small for convenient usage
- Numerical values of multipliers can be interchanged with prefixes

**Ex.** 1 mL =  $10^{-3}$  L

- 1 km = 1000 m
- 1 ng =  $10^{-9}$  g
- 1,130,000,000 s =  $1.13 \times 10^9$  s = 1.13 Gs

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

8

## Laboratory Measurements

### Four common

- Distance ( $d$ )
- Volume
- Mass
- Temperature

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

9

## Laboratory Measurements

### 1. Distance (*d*)

- SI Unit is **meter (m)**
- Meter too large for most laboratory measurements
- Commonly use
  - **Centimeter (cm)**
    - $1\text{ cm} = 10^{-2}\text{ m} = 0.01\text{ m}$
  - **Millimeter (mm)**
    - $1\text{ mm} = 10^{-3}\text{ m} = 0.001\text{ m}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

10

---

---

---

---

---

---

---

### 2. Volume (*V*)

- Dimensions of ( $\text{dm}^3$ )
- SI unit for Volume =  $\text{m}^3$
- Most laboratory measurements use *V* in liters (L)
  - $1\text{ L} = 1\text{ dm}^3$  (exactly)
- Chemistry glassware marked in L or mL
  - $1\text{ L} = 1000\text{ mL}$
- What is a mL?
  - $1\text{ mL} = 1\text{ cm}^3$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

11

---

---

---

---

---

---

---

### 3. Mass

- SI unit is **kilogram (kg)**
- Frequently use grams (g) in laboratory as more realistic size
- $1\text{ kg} = 1000\text{ g}$       $1\text{ g} = 0.001\text{ kg} = \frac{1}{1000}\text{ kg}$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

12

---

---

---

---

---

---

---

## 4. Temperature

### A. Celsius scale

- Most common for use in science
- Water freezes at 0 °C
- Water boils at 100 °C
- 100 degree units between melting and boiling points of water



Michael Watson

---

---

---

---

---

---

---

---

## 4. Temperature

### B. Kelvin scale

- SI unit of temperature is **kelvin (K)**
- Water freezes at 273.15 K and boils at 373.15 K
  - 100 degree units between melting and boiling points

#### Absolute Zero

- Zero point on Kelvin scale
- 0 K = - 273.15 °C

---

---

---

---

---

---

---

---

## Temperature Conversions

- Must convert to Kelvin scale

$$T_K = (t_C + 273.15^\circ\text{C}) \frac{1\text{K}}{1^\circ\text{C}}$$

- **Ex.** What is the Kelvin temperature of a solution at 25 °C?

$$T_K = (25^\circ\text{C} + 273.15^\circ\text{C}) \frac{1\text{K}}{1^\circ\text{C}} = \mathbf{298\text{ K}}$$

---

---

---

---

---

---

---

---

## Learning Check: T Conversions

**Ex. Convert 77 K to the Celsius scale.**

$$T_K = (t_C + 273.15^\circ\text{C}) \frac{1\text{K}}{1^\circ\text{C}} \quad t_C = (T_K - 273.15\text{K}) \frac{1^\circ\text{C}}{1\text{K}}$$

$$t_C = (77\text{K} - 273.15\text{K}) \frac{1^\circ\text{C}}{1\text{K}} = \mathbf{-196^\circ\text{C}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

16

---

---

---

---

---

---

---

**Table 2.2 Some Non-SI Metric Units Commonly Used in Chemistry**

Measurement	Name	Symbol	Value in SI Units
Length	angstrom	Å	1 Å = 0.1 nm = $10^{-10}$ m
Mass	atomic mass unit	u (amu)	1 u = $1.66054 \times 10^{-27}$ kg, approximately
	metric ton	t	1 t = $10^3$ kg
Time	minute	min.	1 min. = 60 s
	hour	h (hr)	1 h = 60 min. = 3600 s
Temperature	degree Celsius	°C	$T_K = t_C + 273.15$
Volume	liter	L	1 L = 1000 cm <sup>3</sup>

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

17

---

---

---

---

---

---

---

## Derived SI Units

- All physical quantities will have units derived from these seven SI base units

**Ex. Area**

- Derived from SI units based on definition of area
- length × width = area
- meter × meter = area  
m × m = m<sup>2</sup>
- SI unit for area = square meters = m<sup>2</sup>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

18

---

---

---

---

---

---

---

## Density

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$d = \frac{m}{V}$$

### Units

- g/mL or g/cm<sup>3</sup>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

19

---

---

---

---

---

---

---

---

## Learning Check

- What is the SI unit for velocity?

$$\text{Velocity } (v) = \frac{\text{distance}}{\text{time}}$$

$$\text{Velocity units} = \frac{\text{meters}}{\text{seconds}} = \frac{\text{m}}{\text{s}}$$

- What is the SI unit for volume of a cube?

$$\text{Volume } (V) = \text{length} \times \text{width} \times \text{height}$$

$$V = \text{meter} \times \text{meter} \times \text{meter}$$

$$V = \text{m}^3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

20

---

---

---

---

---

---

---

---

## More Derived Units

Quantity	Definition	Units
Area	Length × width	m <sup>2</sup>
Volume	Length × width × height	m <sup>3</sup>
Density	Mass / volume	kg/m <sup>3</sup> , g/cm <sup>3</sup> , g/mL
Speed	Distance / time	m s <sup>-1</sup>
Acceleration	Change in speed / time	m s <sup>-2</sup>
Frequency	Event / time	s <sup>-1</sup>
Force	Mass × acceleration	kg m s <sup>-2</sup> (newton, N)
Pressure	Force / area	kg m <sup>-1</sup> s <sup>-2</sup> (pascal, Pa)
Energy	Force × distance	kg m <sup>2</sup> s <sup>-2</sup> (joule, J)

21  
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

---

---

---

---

---

---

---

---

# Stoichiometry

## Stoichiometric Calculations

- Conversions from one set of units to another using Dimensional Analysis

$$m = n \times MM$$

$$N = n \times N_A$$

m: mass, n: amount (mol), MM: molar mass,  
N: number of particles,  $N_A$ : Avogadro's no

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

22

---

---

---

---

---

---

---

## The Mole

- Number of atoms in exactly 12 grams of  $^{12}\text{C}$  atoms

**Ex. How many atoms in 1 mole of  $^{12}\text{C}$  ?**

- Based on experimental evidence

**1 mole of  $^{12}\text{C}$  =  $6.022 \times 10^{23}$  atoms = 12.011 g**

**Avogadro's number =  $N_A$**

- 1 mole of X =  $6.022 \times 10^{23}$  units of X**
- Number of atoms, molecules or particles in one mole
  - 1 mole Xe =  $6.022 \times 10^{23}$  Xe atoms
  - 1 mole  $\text{NO}_2$  =  $6.022 \times 10^{23}$   $\text{NO}_2$  molecules

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

23

---

---

---

---

---

---

---

## Moles of Compounds

### Atoms

- Atomic Mass**
  - Mass of atom (from periodic table)
- 1 mole of atoms = gram atomic mass**  
**=  $6.022 \times 10^{23}$  atoms**

### Molecules

- Molecular Mass**
  - Sum of atomic masses of all atoms in compound's formula
- 1 mole of molecule X = gram molecular mass of X**  
**=  $6.022 \times 10^{23}$  molecules**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

24

---

---

---

---

---

---

---



## Moles of Compounds

### Ionic compounds

#### Formula Mass

- Sum of atomic masses of all atoms in ionic compound's formula

**1 mole ionic compound X = gram formula mass of X**  
**=  $6.022 \times 10^{23}$  formula units**

### General

#### Molar mass (MM)

- Mass of 1 mole of substance (element, molecule, or ionic compound) under consideration

**1 mol of X = gram molar mass of X**  
**=  $6.022 \times 10^{23}$  formula units**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

25

---

---

---

---

---

---

---

---

## SI Unit for Amount = Mole

**1 mole of substance X = gram molar mass of X**

- 1 mole S = 32.06 g S
- 1 mole NO<sub>2</sub> = 46.01 g NO<sub>2</sub>
- Molar mass is our conversion factor between g & moles



**1 mole of X =  $6.022 \times 10^{23}$  units of X**

- N<sub>A</sub> is our conversion factor between moles & molecules



1 mole H<sub>2</sub>O =  $6.022 \times 10^{23}$  molecules H<sub>2</sub>O

1 mole NaCl =  $6.022 \times 10^{23}$  formula units NaCl

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

26

---

---

---

---

---

---

---

---

## Learning Check: Using Molar Mass

**Ex.** How many moles of iron (Fe) are in 15.34 g Fe?

- What do we know?

1 mol Fe = 55.85 g Fe

- What do we want to determine?

15.34 g Fe = ? Mol Fe

Start → End

- Set up ratio so that what you want is on top & what you start with is on the bottom

$$15.34 \text{ g Fe} \times \left( \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} \right) = 0.2747 \text{ mole Fe}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

27

---

---

---

---

---

---

---

---

## Learning Check: Using Molar Mass

**Ex.** If we need 0.168 mole  $\text{Ca}_3(\text{PO}_4)_2$  for an experiment, how many grams do we need to weigh out?

▪ Calculate MM of  $\text{Ca}_3(\text{PO}_4)_2$

$$3 \times \text{mass Ca} = 3 \times 40.08 \text{ g} = 120.24 \text{ g}$$

$$2 \times \text{mass P} = 2 \times 30.97 \text{ g} = 61.94 \text{ g}$$

$$8 \times \text{mass O} = 8 \times 16.00 \text{ g} = 128.00 \text{ g}$$

$$1 \text{ mole } \text{Ca}_3(\text{PO}_4)_2 = 310.18 \text{ g } \text{Ca}_3(\text{PO}_4)_2$$

▪ What do we want to determine?

$$0.168 \text{ g } \text{Ca}_3(\text{PO}_4)_2 = ? \text{ Mol Fe}$$

Start → ← End

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

28

## Learning Check: Using Molar Mass

$$0.160 \text{ mol } \text{Ca}_3(\text{PO}_4)_2 \times \left( \frac{310.18 \text{ g } \text{Ca}_3(\text{PO}_4)_2}{1 \text{ mol } \text{Ca}_3(\text{PO}_4)_2} \right)$$

$$= 52.11 \text{ g } \text{Ca}_3(\text{PO}_4)_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

29

## Your Turn!

**Ex.** How many moles of  $\text{CO}_2$  are there in 10.0 g?

A. 1.00 mol

B. 0.0227 mol

C. 4.401 mol

D. 44.01 mol

E. 0.227 mol

Molar mass of  $\text{CO}_2$

$$1 \times 12.01 \text{ g} = 12.01 \text{ g C}$$

$$2 \times 16.00 \text{ g} = 32.00 \text{ g O}$$

$$1 \text{ mol } \text{CO}_2 = 44.01 \text{ g } \text{CO}_2$$

$$n = m / \text{MM} \quad 10.0 \text{ g } \text{CO}_2 \left( \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \right)$$

$$= 0.227 \text{ mol } \text{CO}_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

30

## Your Turn!

**Ex.** How many grams of platinum (Pt) are in 0.475 mole Pt?

A. 195 g                      Molar mass of Pt = 195.08 g/mol

B. 0.0108 g

C. 0.000513 g

D. 0.00243 g

E. 92.7 g

$$0.475 \cancel{\text{mol Pt}} \times \left( \frac{195.08 \text{ g Pt}}{1 \cancel{\text{mol Pt}}} \right)$$

$$= 92.7 \text{ g Pt}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

31

---

---

---

---

---

---

---

---

**Ex.** How many silver atoms are in a 85.0 g silver bracelet?

▪ What do we know?

$$107.87 \text{ g Ag} = 1 \text{ mol Ag}$$

$$1 \text{ mol Ag} = 6.022 \times 10^{23} \text{ Ag atoms}$$

▪ What do we want to determine?

$$85.0 \text{ g silver} = ? \text{ atoms silver}$$

**g Ag → mol Ag → atoms Ag**

$$85.0 \cancel{\text{g Ag}} \times \left( \frac{1 \cancel{\text{mol Ag}}}{107.87 \cancel{\text{g Ag}}} \right) \times \left( \frac{6.022 \times 10^{23} \text{ atoms Ag}}{1 \cancel{\text{mol Ag}}} \right)$$

$$= 4.7 \times 10^{23} \text{ Ag atoms}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

32

---

---

---

---

---

---

---

---

## Using Avogadro's Number

**Ex.** What is the mass, in grams, of one molecule of octane,  $\text{C}_8\text{H}_{18}$ ?

**Molecules octane → mol octane → g octane**

**1. Calculate molar mass of octane**

$$\text{Mass C} = 8 \times 12.01 \text{ g} = 96.08 \text{ g}$$

$$\text{Mass H} = 18 \times 1.008 \text{ g} = 18.14 \text{ g}$$

$$1 \text{ mol octane} = 114.22 \text{ g octane}$$

**2. Convert 1 molecule of octane to grams**

$$\left( \frac{114.22 \text{ g octane}}{1 \cancel{\text{mol octane}}} \right) \times \left( \frac{1 \cancel{\text{mol octane}}}{6.022 \times 10^{23} \text{ molecules octane}} \right)$$

$$= 1.897 \times 10^{-22} \text{ g octane}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

33

---

---

---

---

---

---

---

---

## Learning Check: Mole Conversions

**Ex.** Calculate the number of formula units of  $\text{Na}_2\text{CO}_3$  in 1.29 moles of  $\text{Na}_2\text{CO}_3$ .

$$1.29 \text{ mol } \text{Na}_2\text{CO}_3 \left( \frac{6.0223 \times 10^{23} \text{ formula units } \text{Na}_2\text{CO}_3}{1 \text{ mol } \text{Na}_2\text{CO}_3} \right) = 7.77 \times 10^{23} \text{ particles } \text{Na}_2\text{CO}_3$$

**Ex.** How many moles of  $\text{Na}_2\text{CO}_3$  are there in  $1.15 \times 10^5$  formula units of  $\text{Na}_2\text{CO}_3$ ?

$$1.15 \times 10^5 \text{ formula units } \text{Na}_2\text{CO}_3 \left( \frac{1 \text{ mol } \text{Na}_2\text{CO}_3}{6.0223 \times 10^{23} \text{ formula units } \text{Na}_2\text{CO}_3} \right) = 1.91 \times 10^{-19} \text{ mol } \text{Na}_2\text{CO}_3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

34

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** How many atoms are in  $1.00 \times 10^{-9}$  g of U? Molar mass U = 238.03 g/mole.

- A.  $6.02 \times 10^{14}$  atoms
- B.  $4.20 \times 10^{11}$  atoms
- C.  $2.53 \times 10^{12}$  atoms
- D.  $3.95 \times 10^{-31}$  atoms
- E.  $2.54 \times 10^{21}$  atoms

$$(1.00 \times 10^{-9} \text{ g U}) \left( \frac{1 \text{ mol U}}{238.03 \text{ g U}} \right) \left( \frac{6.022 \times 10^{23} \text{ atoms U}}{1 \text{ mol U}} \right) = 2.53 \times 10^{12} \text{ atoms U}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

35

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Calculate the mass in grams of  $\text{FeCl}_3$  in  $1.53 \times 10^{23}$  formula units. (molar mass = 162.204 g/mol)

- A. 162.2 g
- B. 0.254 g
- C.  $1.661 \times 10^{-22}$  g
- D. 41.2 g
- E.  $2.37 \times 10^{-22}$

$$1.53 \times 10^{23} \text{ units } \text{FeCl}_3 \left( \frac{1 \text{ mol } \text{FeCl}_3}{6.022 \times 10^{23} \text{ units } \text{FeCl}_3} \right) \times \left( \frac{162.2 \text{ g } \text{FeCl}_3}{1 \text{ mol } \text{FeCl}_3} \right) = 41.2 \text{ g } \text{FeCl}_3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

36

---

---

---

---

---

---

---

---

## Mole-to-Mole Conversion Factors

In H<sub>2</sub>O there are:

- 2 mol H  $\Leftrightarrow$  1 mol H<sub>2</sub>O
- 1 mol O  $\Leftrightarrow$  1 mol H<sub>2</sub>O
- 2 mol H  $\Leftrightarrow$  1 mol O
- on atomic scale
  - 2 atom H  $\Leftrightarrow$  1 molecule H<sub>2</sub>O
  - 1 atom O  $\Leftrightarrow$  1 molecule H<sub>2</sub>O
  - 2 atom H  $\Leftrightarrow$  1 molecule O

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

37

---

---

---

---

---

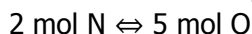
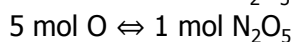
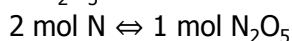
---

---

---

## Stoichiometric Equivalencies

**Ex.** N<sub>2</sub>O<sub>5</sub>



Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

38

---

---

---

---

---

---

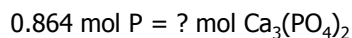
---

---

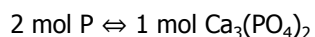
## Calculating the Amount of a Compound by Analyzing One Element

**Ex.** sample is found to contain 0.864 moles of phosphorus P. How many moles of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> are in that sample?

- What do we want to find?



- What do we know?



- **Solution**  $0.864 \text{ mol P} \left( \frac{1 \text{ mol Ca}_3(\text{PO}_4)_2}{2 \text{ mol P}} \right)$   
 $= 0.432 \text{ mol Ca}_3(\text{PO}_4)_2$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

39

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Calculate the number of **moles** of calcium in 2.53 moles of  $\text{Ca}_3(\text{PO}_4)_2$

- A. 2.53 mol Ca
- B. 0.432 mol Ca
- C. 3.00 mol Ca
- D. 7.59 mol Ca
- E. 0.843 mol Ca

$$2.53 \text{ moles of } \text{Ca}_3(\text{PO}_4)_2 = ? \text{ mol Ca}$$

$$3 \text{ mol Ca} \Leftrightarrow 1 \text{ mol } \text{Ca}_3(\text{PO}_4)_2$$

$$2.53 \text{ mol } \text{Ca}_3(\text{PO}_4)_2 \left( \frac{3 \text{ mol Ca}}{1 \text{ mol } \text{Ca}_3(\text{PO}_4)_2} \right)$$

$$= 7.59 \text{ mol Ca}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

40

---

---

---

---

---

---

---

---

## Mass-to-Mass Calculations

**Ex.** Chlorophyll, the green pigment in leaves, has the formula  $\text{C}_{55}\text{H}_{72}\text{MgN}_4\text{O}_5$ . If 0.0011 g of Mg is available to a plant for chlorophyll synthesis, how many grams of carbon will be required to completely use up the magnesium?

### Analysis

$$0.0011 \text{ g Mg} \Leftrightarrow ? \text{ g C}$$

$$0.0011 \text{ g Mg} \rightarrow \text{mol Mg} \rightarrow \text{mol C} \rightarrow \text{g C}$$

### Assembling the tools

$$24.3050 \text{ g Mg} = 1 \text{ mol Mg}$$

$$1 \text{ mol Mg} \Leftrightarrow 55 \text{ mol C}$$

$$1 \text{ mol C} = 12.011 \text{ g C}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

41

---

---

---

---

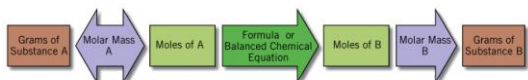
---

---

---

---

## Ex. Mass-to-Mass Conversion



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

$$1 \text{ mol Mg} \Leftrightarrow 24.3 \text{ g Mg}$$

$$1 \text{ mol C} \Leftrightarrow 12.0 \text{ g C}$$

$$0.0011 \text{ g Mg} \rightarrow \text{mol Mg} \rightarrow \text{mol C} \rightarrow \text{g C}$$

$$1 \text{ mol Mg} \Leftrightarrow 55 \text{ mol C}$$

$$0.0011 \text{ g Mg} \times \left( \frac{1 \text{ mol Mg}}{24.3 \text{ g Mg}} \right) \times \left( \frac{55 \text{ mol C}}{1 \text{ mol Mg}} \right) \times \left( \frac{12.0 \text{ g C}}{1 \text{ mol C}} \right)$$

$$= 0.030 \text{ g C}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

42

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** How many g of iron are required to use up all of 25.6 g of oxygen atoms (O) to form  $\text{Fe}_2\text{O}_3$ ?

- A. 59.6 g     **mass O  $\rightarrow$  mol O  $\rightarrow$  mol Fe  $\rightarrow$  mass Fe**
- B. 29.8 g     **25.6 g O  $\rightarrow$  ? g Fe**
- C. 89.4 g     **3 mol O  $\leftrightarrow$  2 mol Fe**
- D. 134 g
- E. 52.4 g

$$25.6 \text{ g O} \times \left( \frac{1 \text{ mol O}}{16.0 \text{ g O}} \right) \times \left( \frac{2 \text{ mol Fe}}{3 \text{ mol O}} \right) \times \left( \frac{55.845 \text{ g Fe}}{1 \text{ mol Fe}} \right) = 59.6 \text{ g Fe}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

43

---

---

---

---

---

---

---

---

## Percentage Composition

- Percentage composition tells us mass of each element in 100.00 g of substance

### Percentage by Mass: %

$$\% \text{ by mass of element} = \frac{\text{mass of element}}{\text{mass of sample}} \times 100\%$$

**Ex.**  $\text{Na}_2\text{CO}_3$  is

- 43.38% Na
- 11.33% C
- 45.29% O
- What is sum of % by mass?     **100.00%**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

44

---

---

---

---

---

---

---

---

## Ex. Percent Composition

**Ex.** A sample of a liquid with a mass of 8.657 g was decomposed into its elements and gave 5.217 g of carbon, 0.9620 g of hydrogen, and 2.478 g of oxygen. What is the percentage composition of this compound?

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

45

---

---

---

---

---

---

---

---

### Ex. % Composition of Compound

$$\text{For C: } \left( \frac{g \text{ C}}{g \text{ total}} \right) \times 100\% = \frac{5.217 \text{ g C}}{8.657 \text{ g}} \times 100\% = 60.26\% \text{ C}$$

$$\text{For H: } \left( \frac{g \text{ H}}{g \text{ total}} \right) \times 100\% = \frac{0.9620 \text{ g H}}{8.657 \text{ g}} \times 100\% = 11.11\% \text{ H}$$

$$\text{For O: } \left( \frac{g \text{ O}}{g \text{ total}} \right) \times 100\% = \frac{2.478 \text{ g O}}{8.657 \text{ g}} \times 100\% = \underline{28.62\% \text{ O}}$$

Sum of percentages: 99.99%

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

46

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** A sample was analyzed and found to contain 0.1417 g nitrogen and 0.4045 g oxygen. What is the percentage composition of this compound?

#### 1. Calculate total mass of sample

$$\text{Total sample mass} = 0.1417 \text{ g} + 0.4045 \text{ g} = 0.5462 \text{ g}$$

#### 2. Calculate % Composition of N

$$\left( \frac{g \text{ N}}{g \text{ total}} \right) \times 100\% = \left( \frac{0.1417 \text{ g N}}{0.5462 \text{ g}} \right) \times 100\% = \underline{25.94\% \text{ N}}$$

#### 3. Calculate % Composition of O

$$\left( \frac{g \text{ O}}{g \text{ total}} \right) \times 100\% = \left( \frac{0.4045 \text{ g O}}{0.5462 \text{ g}} \right) \times 100\% = \underline{74.06\% \text{ O}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

47

---

---

---

---

---

---

---

---

### Ex. Using Percent Composition

Are the mass percentages 30.54% N & 69.46% O consistent with the formula  $\text{N}_2\text{O}_4$ ?

#### Procedure:

1. Assume 1 mole of compound
2. Subscripts tell how many moles of each element are present
  - 2 mol N & 4 mol O
3. Use molar masses of elements to determine mass of each element in 1 mole
  - Molar Mass of  $\text{N}_2\text{O}_4 = 92.14 \text{ g N}_2\text{O}_4 / 1 \text{ mol}$
4. Calculate % by mass of each element

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

48

---

---

---

---

---

---

---

---



$$2 \text{ mol N} \times \frac{14.07 \text{ g N}}{1 \text{ mol N}} = 28.14 \text{ g N}$$
$$4 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 64.00 \text{ g O}$$
$$\% \text{N} = \frac{28.14 \text{ g N}}{92.14 \text{ g N}_2\text{O}_4} \times 100\% = 30.54\% \text{ N in N}_2\text{O}_4$$
$$\% \text{O} = \frac{64.00 \text{ g O}}{92.14 \text{ g N}_2\text{O}_4} \times 100\% = 69.46\% \text{ O in N}_2\text{O}_4$$

- Jeppesen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E 49

---

---

---

---

---

---

**Ex.** If a sample containing only phosphorous & oxygen has percent composition 56.34% P & 43.66% O, is this  $P_4O_{10}$ ?  $4 \text{ mol P} \Leftrightarrow 1 \text{ mol } P_4O_{10}$

$$\%P = \frac{123.9g P}{283.9g P_4O_{10}} \times 100\% = 43.64 \% P$$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter 6E 50

---

---

---

---

---

---

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E 51

---

---

---

---

---

## Strategy for Determining Empirical Formulas

1. Determine mass in **g** of each element
2. Convert mass in **g** to **moles**
3. Divide all quantities by smallest number of moles to get smallest ratio of moles
4. Convert any non-integers into integer numbers.
  - If number ends in decimal equivalent of fraction, multiply all quantities by least common denominator
  - Otherwise, round numbers to nearest integers

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

52

---

---

---

---

---

---

---

---

### 1. Empirical Formula from Mass Data

**Ex.** When a 0.1156 g sample of a compound was analyzed, it was found to contain 0.04470 g of C, 0.01875 g of H, and 0.05215 g of N. Calculate the empirical formula of this compound.

**Step 1:** Calculate moles of each substance

$$0.04470 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 3.722 \times 10^{-3} \text{ mol C}$$

$$0.01875 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 1.860 \times 10^{-2} \text{ mol H}$$

$$0.05215 \text{ g N} \times \frac{1 \text{ mol N}}{14.0067 \text{ g N}} = 3.723 \times 10^{-3} \text{ mol N}$$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

53

---

---

---

---

---

---

---

---

### 1. Empirical Formula from Mass Data

**Step 2:** Select the smallest # of moles.

- Lowest is  $3.722 \times 10^{-3}$  mole

	Mole ratio	Integer ratio
▪ C = $\frac{3.722 \times 10^{-3} \text{ mol C}}{3.722 \times 10^{-3} \text{ mol C}}$	= 1.000	= 1

▪ H = $\frac{1.860 \times 10^{-2} \text{ mol H}}{3.722 \times 10^{-3} \text{ mol C}}$	= 4.997	= 5
---	---------	-----

▪ N = $\frac{3.723 \times 10^{-3} \text{ mol N}}{3.722 \times 10^{-3} \text{ mol C}}$	= 1.000	= 1
---	---------	-----

**Step 3:** Divide all # of moles by the smallest one

**Empirical formula = CH<sub>5</sub>N**

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

54

---

---

---

---

---

---

---

---

## Empirical Formula from Mass Composition

**Ex.** One of the compounds of iron Fe and oxygen O, When a 2.448 g sample was analyzed it was found to have 1.771 g of Fe and 0.677 g of O. Calculate the empirical formula of this compound.

Assembling the tools:

$$1 \text{ mol Fe} = 55.845 \text{ g Fe} \quad 1 \text{ mol O} = 16.00 \text{ g O}$$

1. Calculate moles of each substance

$$1.771 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.845 \text{ g Fe}} = 0.03171 \text{ mol Fe}$$

$$0.677 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 0.0423 \text{ mol O}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

55

---

---

---

---

---

---

---

---

## 1. Empirical Formula from Mass Data

2. Divide both by smallest #mol to get smallest whole # ratio.

$$\frac{0.03171 \text{ mol Fe}}{0.03171 \text{ mol Fe}} = 1.000 \text{ Fe} \times 3 = 3.000 \text{ Fe}$$

$$\frac{0.0423 \text{ mol O}}{0.03171 \text{ mol Fe}} = 1.33 \text{ O} \times 3 = 3.99 \text{ O}$$

$$\text{Or } \frac{\text{Fe}_{0.03171} \text{O}_{0.0423}}{0.03171 \quad 0.03171} = \text{Fe}_{1.00} \text{O}_{1.33}$$

$$\text{Fe}_{(1.00 \times 3)} \text{O}_{(1.33 \times 3)} = \text{Fe}_3 \text{O}_{3.99}$$

**Empirical Formula = Fe<sub>3</sub>O<sub>4</sub>**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

56

---

---

---

---

---

---

---

---

## 2. Empirical Formula from % Composition

**Ex.** Calculate the empirical formula of a compound whose % composition data is 43.64 % P and 56.36 % O. If the molar mass is determined to be 283.9 g/mol, what is the molecular formula?

**Step 1:** Assume 100 g of compound.

▪ 43.64 g P      1 mol P = 30.97 g

▪ 56.36 g O      1 mol O = 16.00 g

$$43.64 \text{ g P} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} = 1.409 \text{ mol P}$$

$$56.36 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.523 \text{ mol P}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

57

---

---

---

---

---

---

---

---

## 2. Empirical Formula from % Composition

**Step 2:** Divide by smallest number of moles

$$\frac{1.409 \text{ mol P}}{1.409 \text{ mol P}} = 1.000 \times 2 = 2$$

$$\frac{3.523 \text{ mol O}}{1.409 \text{ mol P}} = 2.500 \times 2 = 5$$

**Step 3:** Multiple by n to get smallest integer ratio

Here  $n = 2$

**Empirical formula =  $\text{P}_2\text{O}_5$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

58

---

---

---

---

---

---

---

---

## Determining Molecular Formula

- Need molecular mass & empirical formula
- Calculate ratio of molecular mass to mass predicted by empirical formula & round to nearest integer

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}}$$

**Ex.** Glucose

Molecular mass is 180.16 g/mol

Empirical formula =  $\text{CH}_2\text{O}$

Empirical formula mass = 30.03 g/mol

$$n = \frac{180.16 \text{ g}}{30.03 \text{ g}} = 6$$

**Molecular formula =  $\text{C}_6\text{H}_{12}\text{O}_6$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

59

---

---

---

---

---

---

---

---

## Learning Check

The empirical formula of a compound is  $\text{P}_2\text{O}_5$ . If the molar mass is determined to be 283.9 g/mol, what is the molecular formula?

**Step 1:** Calculate empirical mass

$$\begin{aligned} \text{empirical mass } \text{P}_2\text{O}_5 &= (2 \times \text{mass P}) + (5 \times \text{mass O}) \\ &= (2 \times 30.97 \text{ g/mol}) + (5 \times 16.00 \text{ g/mol}) \\ &= (61.94 + 80.00) \text{ g/mol} \\ &= 141.94 \text{ g/mol P}_2\text{O}_5 \end{aligned}$$

**Step 2:** Calculate ratio of molecular to empirical mass

$$n = \frac{283.9 \text{ g/mol}}{141.94 \text{ g/mol}} = 2 \quad \text{Molecular formula} = \text{P}_4\text{O}_{10}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

60

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** The empirical formula of hydrazine is  $\text{NH}_2$ , and its molecular mass is 32.0. What is its molecular formula?

- A.  $\text{NH}_2$   
 B.  $\text{N}_2\text{H}_4$   
 C.  $\text{N}_3\text{H}_6$   
 D.  $\text{N}_4\text{H}_8$   
 E.  $\text{N}_{1.5}\text{H}_3$

$$\begin{aligned}\text{Molar mass of } \text{NH}_2 &= \\ (1 \times 14.01)\text{g} + (2 \times 1.008)\text{g} &= 16.017\text{g} \\ n &= (32.0/16.02) = 2\end{aligned}$$

**Atomic Mass:** N:14.007; H:1.008; O:15.999

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

61

---

---

---

---

---

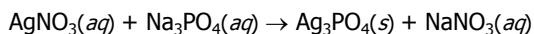
---

---

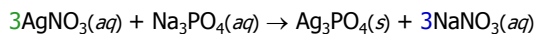
---

## Learning Check: Balancing Equations

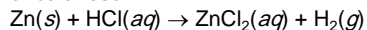
unbalanced



▪ balanced



unbalanced



Balanced



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

62

---

---

---

---

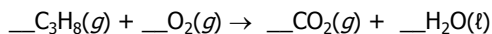
---

---

---

---

## Balance by Inspection



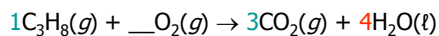
Assume 1 in front of  $\text{C}_3\text{H}_8$

3C

1C  $\times$  3

8H

2H  $\times$  4

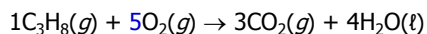


2O  $\times$  5 = 10

O = (3  $\times$  2) + 4 = 10

8H

H = 2  $\times$  4 = 8



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

63

---

---

---

---

---

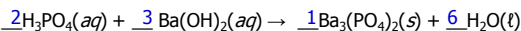
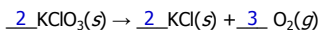
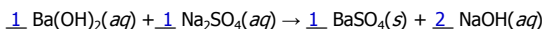
---

---

---

## Your Turn!

**Ex.** Balance each of the following equations.  
What are the coefficients in front of each compound?



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

64

---

---

---

---

---

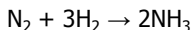
---

---

---

## Stoichiometric Ratios

- Consider the reaction



- Could be read as:

"When 1 **molecule** of nitrogen reacts with 3 **molecules** of hydrogen, 2 **molecules** of ammonia are formed."

### •Molecular relationships

- 1 molecule N<sub>2</sub> ⇔ 2 molecule NH<sub>3</sub>
- 3 molecule H<sub>2</sub> ⇔ 2 molecule NH<sub>3</sub>
- 1 molecule N<sub>2</sub> ⇔ 3 molecule H<sub>2</sub>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

65

---

---

---

---

---

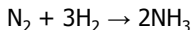
---

---

---

## Stoichiometric Ratios

- Consider the reaction



- Could also be read as:

"When 1 **mole** of nitrogen reacts with 3 **moles** of hydrogen, 2 **moles** of ammonia are formed."

- **Molar relationships**

- 1 mole N<sub>2</sub> ⇔ 2 mole NH<sub>3</sub>
- 3 mole H<sub>2</sub> ⇔ 2 mole NH<sub>3</sub>
- 1 mole N<sub>2</sub> ⇔ 3 mole H<sub>2</sub>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

66

---

---

---

---

---

---

---

---

## Using Stoichiometric Ratios

**Ex.** For the reaction  $\text{N}_2 + 3 \text{H}_2 \rightarrow 2\text{NH}_3$ , how many moles of  $\text{N}_2$  are used when 2.3 moles of  $\text{NH}_3$  are produced?

▪ **Assembling the tools**

- 2 moles  $\text{NH}_3 = 1$  mole  $\text{N}_2$
- 2.3 mole  $\text{NH}_3 = ?$  moles  $\text{N}_2$

$$2.3 \text{ mol NH}_3 \left( \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} \right) = 1.2 \text{ mol N}_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

67

---

---

---

---

---

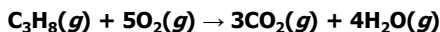
---

---

---

## Your Turn!

**Ex.** If 0.575 mole of  $\text{CO}_2$  is produced by the combustion of propane,  $\text{C}_3\text{H}_8$ , how many moles of oxygen are consumed?



- A. 0.575 mole
- B. 2.88 mole
- C. 0.192 mole
- D. 0.958 mole
- E. 0.345 mole

**Assembling the tools**

- 0.575 mole  $\text{CO}_2 = ?$  moles  $\text{O}_2$
- 3 moles  $\text{CO}_2 = 5$  mole  $\text{O}_2$

$$0.575 \text{ mol CO}_2 \left( \frac{5 \text{ mol O}_2}{3 \text{ mol CO}_2} \right) = 0.958 \text{ mol O}_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

68

---

---

---

---

---

---

---

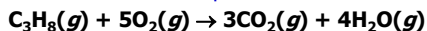
---

## Using Balanced Equation to Determine Stoichiometry

**Ex.** What mass of  $\text{O}_2$  will react with 96.1 g of propane ( $\text{C}_3\text{H}_8$ ) gas, to form gaseous carbon dioxide & water?

**Strategy**

1. Write the balanced equation



2. Assemble the tools

$$96.1 \text{ g C}_3\text{H}_8 \rightarrow \text{moles C}_3\text{H}_8 \rightarrow \text{moles O}_2 \rightarrow \text{g O}_2$$

$$1 \text{ mol C}_3\text{H}_8 = 44.1 \text{ g C}_3\text{H}_8$$

$$1 \text{ mol O}_2 = 32.00 \text{ g O}_2$$

$$1 \text{ mol C}_3\text{H}_8 = 5 \text{ mol O}_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

69

---

---

---

---

---

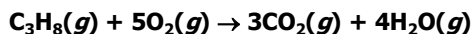
---

---

---

## Using Balanced Equation to Determine Stoichiometry

**Ex.** What mass of  $O_2$  will react with 96.1 g of propane in a complete combustion?



3. Assemble conversions so units cancel correctly

$$96.1 \text{ g } C_3H_8 \times \frac{1 \text{ mol } C_3H_8}{44.1 \text{ g } C_3H_8} \times \frac{5 \text{ mol } O_2}{1 \text{ mol } C_3H_8} \times \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2}$$

**= 349 g of  $O_2$  are needed**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

70

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** How many grams of  $Al_2O_3$  are produced when 41.5 g Al react?



- A. 78.4 g
- B. 157 g
- C. 314 g
- D. 22.0 g
- E. 11.0 g

$$41.5 \text{ g Al} \left( \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \right) \left( \frac{1 \text{ mol } Al_2O_3}{2 \text{ mol Al}} \right) \left( \frac{101.96 \text{ g } Al_2O_3}{1 \text{ mol } Al_2O_3} \right)$$

**= 78.4 g  $Al_2O_3$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

71

---

---

---

---

---

---

---

---

## Limiting Reactant

- Reactant that is completely used up in the reaction
- Present in lower # of moles
- It determines the amount of product produced
- For this reaction = ethylene

### Excess reactant

- Reactant that has some amount left over at end
- Present in higher # of moles
- For this reaction = water

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

72

---

---

---

---

---

---

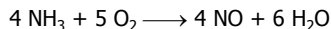
---

---



### Ex. Limiting Reactant Calculation

How many grams of NO can form when 30.0 g NH<sub>3</sub> and 40.0 g O<sub>2</sub> react according to:



Solution: Step 1

mass NH<sub>3</sub> → mole NH<sub>3</sub> → mole O<sub>2</sub> → mass O<sub>2</sub>

Assembling the tools

- 1 mol NH<sub>3</sub> = 17.03 g
  - 1 mol O<sub>2</sub> = 32.00 g
  - 4 mol NH<sub>3</sub> ⇌ 5 mol O<sub>2</sub>
- Only have 40.0 g O<sub>2</sub>,  
O<sub>2</sub> limiting reactant

$$30.0 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{5 \text{ mol O}_2}{4 \text{ mol NH}_3} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2} = 70.5 \text{ g O}_2 \text{ needed}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

73

---

---

---

---

---

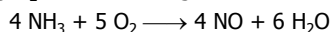
---

---

---

### Ex. Limiting Reactant Calculation

How many grams of NO can form when 30.0 g NH<sub>3</sub> and 40.0 g O<sub>2</sub> react according to:



Solution: Step 2

mass O<sub>2</sub> → mole O<sub>2</sub> → mole NO → mass NO

Assembling the tools

Can only form 30.0 g NO.

- 1 mol O<sub>2</sub> = 32.00 g
- 1 mol NO = 30.01 g
- 5 mol O<sub>2</sub> ⇌ 4 mol NO

$$40.0 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.00 \text{ g O}_2} \times \frac{4 \text{ mol NO}}{5 \text{ mol O}_2} \times \frac{30.01 \text{ g NO}}{1 \text{ mol NO}} = 30.0 \text{ g NO formed}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

74

---

---

---

---

---

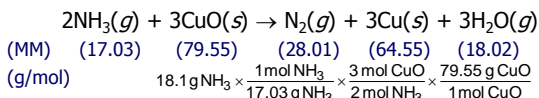
---

---

---

### Your Turn!

Ex. If 18.1 g NH<sub>3</sub> is reacted with 90.4 g CuO, what is the maximum amount of Cu metal that can be formed?



- A. 127 g
- B. 103 g
- C. 72.2 g
- D. 108 g
- E. 56.5 g

127 g CuO needed.

Only have 90.4g so CuO limiting

$$90.4 \text{ g CuO} \times \frac{1 \text{ mol CuO}}{79.55 \text{ g CuO}} \times \frac{3 \text{ mol Cu}}{3 \text{ mol CuO}} \times \frac{63.546 \text{ g Cu}}{1 \text{ mol Cu}}$$

72.2 g Cu can be formed

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

75

---

---

---

---

---

---

---

---

## Theoretical vs. Actual Yield

- **Theoretical Yield**
  - Maximum amount of product that must be obtained if no losses occur.
  - Amount of product formed if all of limiting reagent is consumed.
- **Actual Yield**
  - Amount of product that is actually isolated at end of reaction.
  - Amount obtained experimentally
  - How much is obtained in mass units or in moles.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

76

---

---

---

---

---

---

---

---

## Percentage Yield

Useful to calculate % yield.

### Percent yield

- Relates the actual yield to the theoretical yield
- It is calculated as:

$$\text{percentage yield} = \left( \frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$$

**Ex.** If a cookie recipe predicts a yield of 36 cookies and yet only 24 are obtained, what is the % yield?

$$\text{percentage yield} = \left( \frac{24}{36} \right) \times 100 = 67\%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

77

---

---

---

---

---

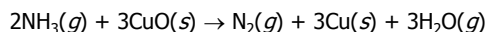
---

---

---

## Ex. Percentage Yield Calculation

When 18.1 g  $\text{NH}_3$  and 90.4 g  $\text{CuO}$  are reacted, the theoretical yield is 72.2 g  $\text{Cu}$ . The actual yield is 58.3 g  $\text{Cu}$ . What is the percent yield?



$$\% \text{ yield} = \frac{58.3 \text{ g Cu}}{72.2 \text{ g Cu}} \times 100\% = 80.7\%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

78

---

---

---

---

---

---

---

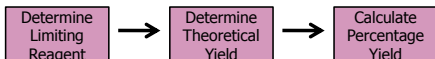
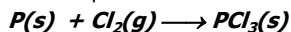
---

## Learning Check: Percentage Yield

**Ex.** A chemist set up a synthesis of solid phosphorus trichloride  $\text{PCl}_3$  by mixing 12.0 g of solid phosphorus with 35.0 g chlorine gas and obtained 42.4 g of solid phosphorus trichloride. Calculate the percentage yield of this compound.

### Analysis:

Write balanced equation



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

79

---

---

---

---

---

---

---

---

## Learning Check: Percentage Yield

### Assembling the Tools:

- 1 mol P = 30.97 g P
- 1 mol  $\text{Cl}_2$  = 70.90 g  $\text{Cl}_2$
- 3 mol  $\text{Cl}_2 \Leftrightarrow$  2 mol P

### Solution

#### 1. Determine Limiting Reactant

$$12.0 \text{ g P} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} \times \frac{3 \text{ mol Cl}_2}{2 \text{ mol P}} \times \frac{70.90 \text{ g Cl}_2}{1 \text{ mol Cl}_2} = 41.2 \text{ g Cl}_2$$

- But you only have 35.0 g  $\text{Cl}_2$ , so  $\text{Cl}_2$  is limiting reactant

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

80

---

---

---

---

---

---

---

---

## Learning Check: Percentage Yield

### Solution

#### 2. Determine Theoretical Yield

$$35.0 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} \times \frac{2 \text{ mol PCl}_3}{3 \text{ mol Cl}_2} \times \frac{137.32 \text{ g PCl}_3}{1 \text{ mol PCl}_3} = 45.2 \text{ g PCl}_3$$

#### 3. Determine Percentage Yield

- Actual yield = 42.4 g

$$\text{percentage yield} = \left( \frac{42.4 \text{ g PCl}_3}{45.2 \text{ g PCl}_3} \right) \times 100 = 93.8 \%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

81

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** When 6.40 g of CH<sub>3</sub>OH was mixed with 10.2 g of O<sub>2</sub> and ignited, 6.12 g of CO<sub>2</sub> was obtained. What was the percentage yield of CO<sub>2</sub>?



MM(g/mol) (32.04) (32.00) (44.01) (18.02)

A. 6.12%

B. 8.79%

C. 100%

D. 142%

E. 69.6%

$$6.40 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \times \frac{3 \text{ mol CO}_2}{2 \text{ mol CH}_3\text{OH}} \times \frac{32.00 \text{ g O}_2}{1 \text{ mol O}_2}$$

= 9.59 g O<sub>2</sub> needed; CH<sub>3</sub>OH limiting

$$6.40 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol CH}_3\text{OH}}{32.04 \text{ g CH}_3\text{OH}} \times \frac{2 \text{ mol CO}_2}{2 \text{ mol CH}_3\text{OH}} \times \frac{44.01 \text{ g CO}_2}{1 \text{ mol CO}_2}$$

= 8.79 g CO<sub>2</sub> in theory

$$\frac{6.12 \text{ g CH}_3\text{OH actual}}{8.79 \text{ g CH}_3\text{OH theory}} \times 100\% = 69.6\%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

82

## Molarity Concentration

- Number of moles of solute per liter of solution.
- Allows us to express relationship between moles of solute and volume of solution
- Hence, 0.100 M solution of NaCl contains 0.100 mole NaCl in 1.00 liter of solution
- Same concentration results if you dissolve 0.0100 mol of NaCl in 0.100 liter of solution

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{mole}}{\text{Volume}}$$

$$\frac{0.100 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}} = \frac{0.0100 \text{ mol NaCl}}{0.100 \text{ L NaCl soln}} = 0.100 \text{ M NaCl}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

83

## Learning Check: Calculating Molarity (from grams and volume)

**Ex.** Calculate the molarity (M) of a solution prepared by dissolving 11.5 g NaOH (40.00 g/mol) solid in enough water to make 1.50 L of solution.

**g NaOH → mol NaOH → M NaOH**

$$11.5 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.288 \text{ mol NaOH}$$

$$M = \frac{\text{moles NaOH}}{\text{L so ln}} = \frac{0.288 \text{ mol NaOH}}{1.50 \text{ L soln}}$$

$$= 0.192 \text{ M NaOH}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

84

## Learning Check: Calculating Volume (from Molarity and moles)

**Ex.** How many mL of 0.250 *M* NaCl solution are needed to obtain 0.100 mol of NaCl?

▪ Use *M* definition

$$0.250 \text{ } M \text{ NaCl} = \frac{0.250 \text{ mol NaCl}}{1.00 \text{ L NaCl soln}}$$

▪ Given molarity and moles, need volume

$$0.100 \text{ mol NaCl} \times \frac{1.00 \text{ L NaCl soln}}{0.250 \text{ mol NaCl}} \times \frac{1000 \text{ mL NaCl soln}}{1 \text{ L NaCl soln}}$$

$$= 400 \text{ mL of } 0.250 \text{ } M \text{ NaCl solution}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

85

## Temperature Insensitive Concentration

### 1. Percent Concentrations

- Also called percent by mass or percent by weight

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

- This is sometimes indicated %(w/w) where "w" stands for weight
- The "(w/w)" is often omitted

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

86

## Ex. Percent by Mass

What is the percent by mass of NaCl in a solution consisting of 12.5 g of NaCl and 75.0 g water?

$$\text{percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

$$\text{wt}\%_{\text{NaCl}} = \frac{12.5 \text{ g}}{(12.5 + 75.0) \text{ g}} \times 100$$

$$\text{wt}\%_{\text{NaCl}} = 14.3\% \text{ NaCl}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

87

## Learning Check

**Ex.** How many grams of sea salt would be needed to prepare 62.5 L of 3.5% w/w solution with density of 1.03 g/mL. ?

▪ What do we need to find?

- 62.5 L  $\Leftrightarrow$  ? g sea salt

▪ What do we know?

- 3.5 g sea salt  $\Leftrightarrow$  100 g solution
- 1.03 g soln  $\Leftrightarrow$  1.00 mL solution
- 1000 mL  $\Leftrightarrow$  1.00 L

$$62.5 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.03 \text{ g soln}}{1.00 \text{ mL soln}} \times \frac{3.5 \text{ g sea salt}}{100 \text{ g soln}}$$

=  $2.2 \times 10^3$  g sea salt

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

88

---

---

---

---

---

---

---

---

## More Temperature Insensitive Concentration Units

### Molality ( $m$ )

- Number of moles of solute per kilogram solvent

$$\text{molality} = m = \frac{\text{mol of solute}}{\text{kg of solvent}}$$

- Also **Molal concentration**
- Independent of temperature

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

89

---

---

---

---

---

---

---

---

## Ex. Concentration Calculation

A. If you prepare a solution by dissolving 25.38 g of  $\text{I}_2$  in 500.0 g of water, what is the molality ( $m$ ) of the solution?

▪ What do we need to find?

- 25.38 g  $\Leftrightarrow$  ?  $m$

▪ What do we know?

- 253.8 g  $\text{I}_2 \Leftrightarrow$  1 mol  $\text{I}_2$
- $m = \text{mol solute/kg solvent}$

- 500.0 g  $\Leftrightarrow$  0.5000 kg

▪ Solve it  $25.38 \text{ g I}_2 \times \frac{1 \text{ mol I}_2}{253.8 \text{ g I}_2} \times \frac{1}{0.5000 \text{ kg water}}$

$$= 0.2000 \text{ mol I}_2/\text{kg water} = \mathbf{0.2000 \text{ } m}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

90

---

---

---

---

---

---

---

---

### Ex. Calculating $M$ from $m$ (cont.)

B. What is the molarity ( $M$ ) of this solution? The density of this solution is 1.59 g/mL.

What do we need to find?

- 25.38 g  $\Leftrightarrow$  ?  $M$

What do we know?

- 253.8 g  $I_2 \Leftrightarrow$  1 mol  $I_2$
- $M = \text{mol solute/L soln}$
- 1.59 g soln  $\Leftrightarrow$  1 mL soln
- g of soln = g  $I_2$  + g  $H_2O$  = 500.0 g + 25.38 g

Solve it

$$25.38 \text{ g } I_2 \times \frac{1 \text{ mol } I_2}{253.8 \text{ g } I_2} \times \frac{1}{525.38 \text{ g soln}} \times \frac{1.59 \text{ g}}{1.00 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$
$$= 0.3030 \text{ mol } I_2/\text{L soln} = \mathbf{0.3030 \text{ M}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

91

### Converting between Concentrations

Ex. Calculate the molarity and the molality of a 40.0% HBr solution. The density of this solution is 1.38 g/mL.

$$40.0\% \text{ HBr} = wt\% = \frac{40.0 \text{ g HBr}}{100 \text{ g solution}} \times 100$$

If we assume 100.0 g of solution, then 40.0 g of HBr.

$$m = \frac{\text{mol HBr}}{\text{kg of } H_2O} \quad \text{mol HBr} = \frac{40.0 \text{ g HBr}}{80.91 \text{ g HBr/mol}} = 0.494 \text{ mol HBr}$$

If 100 g solution, then

$$\text{mass } H_2O = 100.0 \text{ g soln} - 40.0 \text{ g HBr} = 60.0 \text{ g } H_2O$$

$$m = \frac{\text{mol HBr}}{\text{kg } H_2O} = \frac{0.494 \text{ mol HBr}}{0.0600 \text{ kg } H_2O} = 8.24 \text{ m}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

92

### Converting between Concentrations (cont.)

Now Calculate Molarity of 40% HBr

$$M = \frac{\text{mol HBr}}{\text{L solution}}$$

$$Vol/\text{Soln} = \frac{\text{mass}}{\text{density}} = \frac{100 \text{ g}}{1.38 \text{ g/mL}} = \mathbf{72.46 \text{ mL}}$$

$$\text{mol/HBr} = 0.494 \text{ mol}$$

$$M = \frac{0.494 \text{ mol HBr}}{72.46 \text{ mL solution}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = \mathbf{6.82 \text{ M}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

93

### Your Turn!

**Ex.** What is the molality of 50.0% (w/w) NaOH solution?

- A. 0.500 *m*
- B. 1.25 *m*
- C. 0.025 *m*
- D. 25 *m*
- E. 50 *m*

100.0 g soln = 50.0 g NaOH + 50.0 g water

$$50.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ m}}{\text{mol/kg}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1}{50.0 \text{ g water}}$$

**= 25 *m***

*MM(g/mol) H<sub>2</sub>O: 18.02; NaOH: 40.00*

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

94

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** What is the molarity of the 50%(w/w) solution if its density is 1.529 g/mL?

- A. 19 *M*
- B. 1.25 *M*
- C. 1.9 *M*
- D. 0.76 *M*

$$50 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.0 \text{ g}} \times \frac{1.529 \text{ g soln}}{\text{mL}}$$

$$\times \frac{1}{100 \text{ g soln}} \times \frac{1000 \text{ mL}}{\text{L}} = 19 \text{ M}$$

or

$$25 \frac{\text{mmol}}{\text{g soln}} \times \frac{50 \text{ g H}_2\text{O}}{100 \text{ g soln}} \times \frac{1.529 \text{ g}}{\text{mL}} = 19 \text{ M}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

95

---

---

---

---

---

---

---

---

### Other Temperature Insensitive Concentration Units

#### ▪ Mole Fraction

$$\chi_A = \frac{\# \text{ mol A}}{\text{Total moles of all components}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

96

---

---

---

---

---

---

---

---



# Chapter 2

## Properties of Gases

Chemistry: The Molecular Nature  
of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

### Properties of Common Gases

- Despite wide differences in chemical properties, ALL gases more or less obey the same set of **physical properties**.

#### Four Physical Properties of Gases

- Pressure (**P**)
- Volume (**V**)
- Temperature (**T**)
- Amount = moles (**n**)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

98

---

---

---

---

---

---

---

### Units of Pressure

**Pascal = Pa**

- SI unit for **Pressure**
- Very small
- $1 \text{ atm} \equiv 101,325 \text{ Pa} = 101 \text{ kPa}$

- $1 \text{ atm}$  too big for most lab work

$$1 \text{ torr} = \frac{1}{760} \text{ atm} \quad 1 \text{ atm} \equiv 760 \text{ mm Hg}$$

At sea level  $1 \text{ torr} = 1 \text{ mm Hg}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

99

---

---

---

---

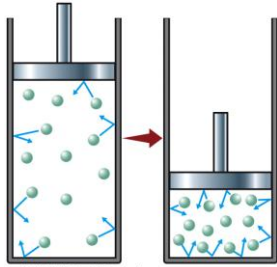
---

---

---

## Boyle's Law

- Studied relationship between  $P$  and  $V$
- Work done at constant  $T$  as well as constant number of moles ( $n$ )
- $T_1 = T_2$
- As  $V \downarrow$ ,  $P \uparrow$



The **volume** of a fixed quantity of gas at constant temperature is **inversely proportional** to the **pressure**.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

100

---

---

---

---

---

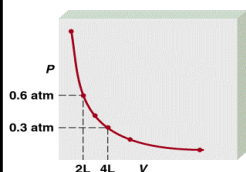
---

---

---

A plot of  $V$  versus  $P$  results in a curve

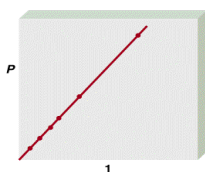
A plot of  $V$  versus  $1/P$  will be a straight line



$P \propto 1/V$

$P \times V = \text{constant}$

$$P_1 \times V_1 = P_2 \times V_2$$



$P = k(1/V)$

This means a plot of  $P$  versus  $1/V$  will be a straight line.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

101

---

---

---

---

---

---

---

---

**Ex:** A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. What is the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL?

$$P_1 \times V_1 = P_2 \times V_2$$

$$P_1 = 726 \text{ mmHg} \quad P_2 = ?$$

$$V_1 = 946 \text{ mL} \quad V_2 = 154 \text{ mL}$$

$$P_2 = \frac{P_1 \times V_1}{V_2} = \frac{726 \text{ mmHg} \times 946 \text{ mL}}{154 \text{ mL}} = 4460 \text{ mmHg}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

102

---

---

---

---

---

---

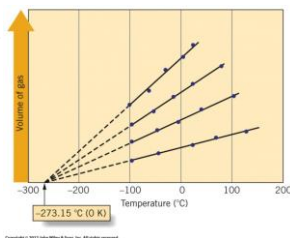
---

---

## Charles's Law

- Charles worked on relationship of how  $V$  changes with  $T$
- Kept  $P$  and  $n$  constant
- Showed  $V \uparrow$  as  $T \uparrow$

• i.e.,  $\frac{V}{T} = k$



- The volume of a fixed amount of gas at constant pressure is directly proportional to its absolute temperature.

$$V_1/T_1 = V_2/T_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

103

- Ex.** Anesthetic gas is normally given to a patient when the room temperature is 20.0 °C and the patient's body temperature is 37.0°C. What would this temperature change do to 1.60 L of gas if the pressure and mass stay the same?

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{1.60 \text{ L} \times 310.15 \text{ K}}{293.15 \text{ K}} \quad V_2 = 1.69 \text{ L}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

104

**Ex:** A sample of carbon monoxide gas occupies 3.20 L at 125 °C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

$$V_1/T_1 = V_2/T_2$$

$$V_1 = 3.20 \text{ L}$$

$$V_2 = 1.54 \text{ L}$$

$$T_1 = 398.15 \text{ K}$$

$$T_2 = ?$$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{1.54 \text{ L} \times 398.15 \text{ K}}{3.20 \text{ L}} = 192 \text{ K}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

105

## Gay-Lussac's Law

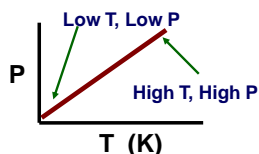
- Volume ( $V$ ) and number of moles ( $n$ ) are constant
- $P \uparrow$  as  $T \uparrow$

$V = \text{constant}$ ,  $n = \text{Constant}$

The **pressure** of a fixed amount of gas at constant volume is **directly proportional** to its **absolute temperature**.

$$P \propto T$$

$$P_1 T_2 = P_2 T_1$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

106

---

---

---

---

---

---

---

---

## Combined Gas Law

- Ratio  $\frac{PV}{T}$
- Constant for fixed amount of gas ( $n$ )
- $\frac{PV}{T} = C$  for fixed amount (moles)

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

107

---

---

---

---

---

---

---

---

## How Other Laws Fit into Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Boyle's Law	$T_1 = T_2$	$P_1 V_1 = P_2 V_2$
Charles' Law	$P_1 = P_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's Law	$V_1 = V_2$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

108

---

---

---

---

---

---

---

---

## Combined Gas Law

- Ex. If a sample of air occupies 500. mL at STP\*, what is the volume at 85 °C and 560 torr?

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{760 \text{ torr} \times 500. \text{ mL}}{273.15 \text{ K}} = \frac{560 \text{ torr} \times V_2}{358.15 \text{ K}}$$

$$= 890 \text{ mL}$$

\*Standard Temperature (273.15K)

Standard Pressure (1 atm)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

109

---

---

---

---

---

---

---

---

## Ex. Using Combined Gas Law

- What will be the final pressure of a sample of nitrogen gas with a volume of 950 m<sup>3</sup> at 745 torr and 25.0 °C if it is heated to 60.0 °C and given a final volume of 1150 m<sup>3</sup>?

$$P_1 = 745 \text{ torr}$$

$$P_2 = ?$$

$$V_1 = 950 \text{ m}^3$$

$$V_2 = 1150 \text{ m}^3$$

$$T_1 = 25.0 \text{ °C} + 273.15$$

$$= 298.15 \text{ K}$$

$$T_2 = 60.0 \text{ °C} + 273.15$$

$$= 333.15 \text{ K}$$

$$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2} = \frac{745 \text{ torr} \times 950 \text{ m}^3 \times 333.15 \text{ K}}{298.15 \text{ K} \times 1150 \text{ m}^3}$$

$$P_2 = 688 \text{ torr}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

110

---

---

---

---

---

---

---

---

## Your Turn!

- Ex. Which units must be used in all gas law calculations?

- K
- atm
- L
- no specific units as long as they cancel

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

111

---

---

---

---

---

---

---

---

## Relationships between Gas Volumes

- In reactions in which products and reactants are gases:
  - If  $T$  and  $P$  are constant
  - Simple relationship among volumes
- hydrogen + chlorine  $\rightarrow$  hydrogen chloride  
 1 vol            1 vol            2 vol
- hydrogen + oxygen  $\rightarrow$  water (gas)  
 2 vol            1 vol            2 vol
- ratios of simple, whole numbers

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

112

---

---

---

---

---

---

---

---

## Avogadro's Principle

- When measured at same  $T$  and  $P$ , equal  $V$ s of gas contain equal number of moles
- Volume of a gas is directly proportional to its number of moles,  $n$
- $V \propto n$  (at constant  $P$  and  $T$ )

	$H_2(g)$	$Cl_2(g)$	$\longrightarrow$	$2 HCl(g)$
Coefficients	1	1		2
Volumes	1	1		2
Molecules	1	1		2 (Avogadro's Principle)
Moles	1	1		2

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

113

---

---

---

---

---

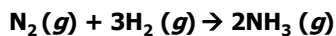
---

---

---

## Learning Check:

**Ex.** Calculate the volume of ammonia formed by the reaction of 25L of hydrogen with excess nitrogen.



$$\frac{25 \text{ L } H_2}{1} \times \frac{2 \text{ L } NH_3}{3 \text{ L } H_2} = 17 \text{ L } NH_3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

114

---

---

---

---

---

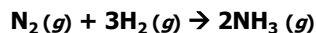
---

---

---

### Learning Check:

If 125 L  $\text{H}_2$  react with 50 L  $\text{N}_2$ , what volume of  $\text{NH}_3$  can be expected?



$$\frac{125 \text{ L H}_2}{1} \times \frac{2 \text{ L NH}_3}{3 \text{ L H}_2} = 83.3 \text{ L NH}_3$$

$$\frac{50 \text{ L N}_2}{1} \times \frac{2 \text{ L NH}_3}{1 \text{ L N}_2} = 100 \text{ L NH}_3$$

**$\text{H}_2$  is limiting reagent 83.3 L**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

115

---

---

---

---

---

---

---

---

### Learning Check:

**Ex.** How many liters of  $\text{N}_2(g)$  at 1.00 atm and 25.0 °C are produced by the decomposition of 150. g of  $\text{NaN}_3$ ?  $2\text{NaN}_3(s) \rightarrow 2\text{Na}(s) + 3\text{N}_2(g)$

$$\frac{150. \text{ g NaN}_3}{1} \times \frac{1 \text{ mol NaN}_3}{65.0099 \text{ g}} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} = 3.461 \text{ mol N}_2$$

$$\frac{3.461 \text{ mol N}_2}{1} \times \frac{22.4 \text{ L}}{1 \text{ mol at STP}} = 77.53 \text{ L}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}; V_2 = \frac{V_1 T_2}{T_1}$$

$$V_2 = \frac{77.53 \text{ L} \times 298.15 \text{ K}}{273.15 \text{ K}} = 84.62 \text{ L}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

116

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** How many liters of  $\text{SO}_3$  will be produced when 25 L of sulfur dioxide reacts with 75 L of oxygen? All gases are at STP.

- A. 25 L  $25 \text{ L SO}_2 \times \frac{2 \text{ L SO}_3}{2 \text{ L SO}_2} = 25 \text{ L SO}_3$   
 B. 50 L  
 C. 100 L  $75 \text{ L O}_2 \times \frac{2 \text{ L SO}_3}{1 \text{ L O}_2} = 150 \text{ L SO}_3$   
 D. 150 L  
 E. 75 L

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

117

---

---

---

---

---

---

---

---

## Ideal Gas Law

- With Combined Gas Law we saw that

$$\frac{PV}{T} = C$$

- With Avogadro's results we see that this is modified to

$$\frac{PV}{T} = n \times R$$

- Where **R** = a new constant = Universal Gas constant

$$PV = nRT$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

118

## Standard Molar Volume

- Volume of 1 mole gas must be identical for all gases under same P and T
- Standard Conditions of Temperature and Pressure — STP
  - STP = 1 atm and 273.15 K (0.0°C)**
    - Under these conditions
    - 1 mole gas occupies  $V = 22.4 \text{ L}$
    - $22.4 \text{ L} \equiv$  standard molar volume

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

119

## What is the value of **R**?

- Plug in values of **T**, **V**, **n** and **P** for 1 mole of gas at STP (1 atm and 0.0°C)

- $T = 0.0^\circ\text{C} = 273.15 \text{ K}$

- $P = 1 \text{ atm}$

- $V = 22.4 \text{ L}$

- $n = 1 \text{ mol}$

Units	Numerical Value
L·atm/mol·K	0.08206
J/mol·K*	8.314
cal/mol·K	1.987
m <sup>3</sup> ·Pa/mol·K*	8.314
L·torr/mol·K	62.36

\*SI unit

$$R = \frac{PV}{nT} = \frac{1\text{atm} \times 22.4\text{L}}{1\text{mol} \times 273.15\text{K}}$$

$$R = 0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

120



## Learning Check:

**Ex.** How many liters of  $N_2(g)$  at 1.00 atm and 25.0 °C are produced by the decomposition of 150. g of  $NaN_3$ ?  $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

$V = ?$

$$V = nRT/P$$

$P = 1 \text{ atm}$

$T = 25^\circ\text{C} + 273.15 = 298.15 \text{ K}$

$$n = \text{mol } N_2 = \frac{150. \text{ g } NaN_3}{1} \times \frac{1 \text{ mol } NaN_3}{65.0099 \text{ g}} \times \frac{3 \text{ mol } N_2}{2 \text{ mol } NaN_3}$$

$$n = 3.461 \text{ mol } N_2$$

$$V = \frac{(3.461 \text{ mol } N_2)(0.082057 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298.15 \text{ K})}{1 \text{ atm}} \quad \mathbf{V = 84.62 \text{ L}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

121

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Solid  $CaCO_3$  decomposes to solid  $CaO$  and  $CO_2$  when heated. What is the pressure, in atm, of  $CO_2$  in a 50.0 L container at 35 °C when 75.0 g of calcium carbonate decomposes?

A. 0.043 atm

B. 0.010 atm

C. 0.38 atm

D. 0.08 atm

E. 38 atm

$$PV = nRT$$

$$P = m \times R \times T / MM \times V$$

$$\frac{75.0 \text{ g } CaCO_3 \times \frac{1 \text{ mol } CaCO_3}{100.1 \text{ g}} \times \frac{1 \text{ mol } CO_2}{1 \text{ mol } CaCO_3} \times 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 308 \text{ K}}{50.0 \text{ L}}$$

$$= 0.38 \text{ atm}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

122

---

---

---

---

---

---

---

---

▪ **Ex.** A gas allowed to flow into a 300 mL gas bulb until the pressure was 685 torr. The sample now weighed 1.45 g; its temperature was 27.0°C. What is the molecular mass of this gas?

$$T = 27.0^\circ\text{C} + 273.15 \text{ K} = 300.2 \text{ K}$$

$$V = 300 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.300 \text{ L}$$

$$P = 685 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.901 \text{ atm}$$

$$n = \frac{PV}{RT} = \frac{0.901 \text{ atm} \times 0.300 \text{ L}}{0.082057 (\text{atm} \cdot \text{L} / \text{mol} \cdot \text{K}) \cdot 300.2 \text{ K}} = 0.01098 \text{ mole}$$

$$MM = \frac{\text{mass}}{n} = \frac{1.45 \text{ g}}{0.01098 \text{ mol}} = 132 \text{ g/mol}$$

Gas = Xe

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

123

---

---

---

---

---

---

---

---

**Ex.** A gaseous compound with an empirical formula of  $\text{PF}_2$  was found to have a density of 5.60 g/L at 23.0 °C and 750 torr. Calculate its molecular mass and its molecular formula.

$$T = 23.0\text{ }^{\circ}\text{C} + 273.15\text{ K} = 296.2\text{ K}$$

$$P = 750\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 0.9868\text{ atm}$$

$$n = \frac{PV}{RT} = \frac{0.9868\text{ atm} \times 1.000\text{ L}}{0.082057(\text{atm} \cdot \text{L} / \text{mol} \cdot \text{K}) \cdot 296.2\text{ K}} = 0.04058\text{ mole}$$

$$MM = \frac{\text{mass}}{n} = \frac{5.60\text{ g}}{0.04058\text{ mol}} = 138\text{ g/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

124

---

---

---

---

---

---

---

---

### Ex. Solution (cont)

- Now to find molecular formula given **empirical formula** and **MM**
- First find mass of empirical formula unit
- $1\text{ P} = 1 \times 31\text{ g/mol} = 31\text{ g/mol}$
- $2\text{ F} = 2 \times 19\text{ g/mol} = 38\text{ g/mol}$
- Mass of  $\text{PF}_2 = 69\text{ g/mol}$

$$MM = \frac{\text{molecular mass}}{\text{empirical mass}} = \frac{138\text{ g/mol}}{69\text{ g/mol}} = 2$$

$\therefore$  the correct molecular formula is  $\text{P}_2\text{F}_4$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

125

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** 7.52 g of a gas with an empirical formula of  $\text{NO}_2$  occupies 2.0 L at a pressure of 1.0 atm and 25 °C. Determine the molar mass and molecular formula of the compound.

- A. 45.0 g/mol,  $\text{NO}_2$
- B. 90.0 g/mol,  $\text{N}_2\text{O}_4$
- C. 7.72 g/mol,  $\text{NO}$
- D. 0.0109 g/mol,  $\text{N}_2\text{O}$
- E. Not enough data to determine molar mass

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

126

---

---

---

---

---

---

---

---

## Your Turn! - Solution

$$MW = \frac{7.52 \text{ g} \times 0.0821 \frac{\text{L atm}}{\text{K mol}} \times 298 \text{ K}}{1.0 \text{ atm} \times 2.0 \text{ L}} = 90.0 \text{ g/mol}$$

$$90 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ mol NO}_2}{45.0 \text{ g}} = \frac{2 \text{ mol NO}_2}{\text{mol}}$$

Molecular formula is N<sub>2</sub>O<sub>4</sub>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

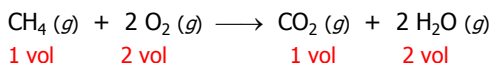
127

## Stoichiometry of Reactions Between Gases

- Can use stoichiometric coefficients in equations to relate volumes of gases

- Provided **T** and **P** are constant
- Volume  $\propto$  moles **V  $\propto$  n**

**Ex.** Methane burns according to the following equation.



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

128

### Ex.

- The combustion of 4.50 L of CH<sub>4</sub> consumes how many liters of O<sub>2</sub>? (Both volumes measured at STP.)
- P** and **T** are all constant so just look at ratio of stoichiometric coefficients

$$\text{Volume of O}_2 = 4.50 \text{ L} * \frac{2 \text{ L O}_2}{1 \text{ L CH}_4}$$

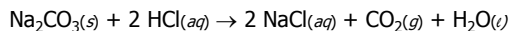
$$= 9.00 \text{ L O}_2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

129

**Ex.** Gas bulb with a volume of 250 mL. How many grams of  $\text{Na}_2\text{CO}_3 (s)$  would be needed to prepare enough  $\text{CO}_2 (g)$  to fill this bulb when the pressure is at 738 torr and the temperature is 23 °C? The equation is:



$$V = 250\text{mL} \times \frac{1\text{L}}{1000\text{mL}} = 0.250\text{L}$$

$$P = 738\text{torr} \times \frac{1\text{atm}}{760\text{torr}} = 0.971\text{atm}$$

$$T = 23.0^\circ\text{C} + 273.15\text{K} = 296.2\text{K}$$

$$n = \frac{PV}{RT} = \frac{0.971\text{atm} \times 0.250\text{L}}{0.082057(\text{atm} \cdot \text{L} / \text{mol} \cdot \text{K}) \cdot 296.2\text{K}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

130

---

---

---

---

---

---

---

---

### Ex. Solution (cont)

$$= 9.989 \times 10^{-3} \text{ mole } \text{CO}_2$$

$$9.989 \times 10^{-3} \text{ mol } \text{CO}_2 \times \frac{1 \text{ mol } \text{Na}_2\text{CO}_3}{1 \text{ mol } \text{CO}_2}$$

$$= 9.989 \times 10^{-3} \text{ mol } \text{Na}_2\text{CO}_3$$

$$9.989 \times 10^{-3} \text{ mol } \text{Na}_2\text{CO}_3 \times \frac{106 \text{ g } \text{Na}_2\text{CO}_3}{1 \text{ mol } \text{Na}_2\text{CO}_3}$$

$$= 1.06 \text{ g } \text{Na}_2\text{CO}_3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

131

---

---

---

---

---

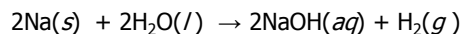
---

---

---

### Your Turn!

**Ex.** How many grams of sodium are required to produce 20.0 L of hydrogen gas at 25.0 °C, and 750 torr ?



- A. 18.6 g
- B. 57.0 g
- C. 61.3 g
- D. 9.62 g
- E. 37.1 g

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

132

---

---

---

---

---

---

---

---

## Your Turn! - Solution

- Moles of H<sub>2</sub> produced:

$$n = \frac{750 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} \times 20.0 \text{ L}}{0.0821 \frac{\text{L atm}}{\text{K mol}} \times 298 \text{ K}} = 0.807 \text{ mol H}_2$$

- Grams of sodium required:

$$\text{g Na} = 0.807 \text{ mol H}_2 \times \frac{2 \text{ mol Na}}{\text{mol H}_2} \times \frac{23.0 \text{ g}}{\text{mol Na}} = 37.1 \text{ g}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

133

---

---

---

---

---

---

---

---

## Dalton's Law of Partial Pressure

- For mixture of non-reacting gases in container
- Total pressure exerted is sum of the individual partial pressures that each gas would exert alone
- **$P_{\text{total}} = P_a + P_b + P_c + \dots$**
- Where  **$P_a$ ,  $P_b$  and  $P_c$**  = partial pressures
- **Partial pressure**
  - Pressure that particular gas would exert if it were alone in container

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

134

---

---

---

---

---

---

---

---

## Dalton's Law of Partial Pressures

- Assuming each gas behaves ideally
- Partial pressure of each gas can be calculated from Ideal Gas Law

$$P_a = \frac{n_a RT}{V} \quad P_b = \frac{n_b RT}{V} \quad P_c = \frac{n_c RT}{V}$$

- So Total Pressure is

$$\begin{aligned} P_{\text{total}} &= P_a + P_b + P_c + \dots \\ &= \frac{n_a RT}{V} + \frac{n_b RT}{V} + \frac{n_c RT}{V} + \dots \end{aligned}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

135

---

---

---

---

---

---

---

---

## Dalton's Law of Partial Pressures

- Rearranging

$$P_{total} = (n_a + n_b + n_c + \dots) \left( \frac{RT}{V} \right)$$

- Or

$$P_{total} = n_{total} \left( \frac{RT}{V} \right)$$

- Where  $n_{total} = n_a + n_b + n_c + \dots$

$n_{total}$  = sum of # moles of various gases in mixture

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

136

---

---

---

---

---

---

---

---

- Ex.** Mixtures of 46 L He at 25 °C and 1.0 atm and 12 L O<sub>2</sub> at 25 °C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25 °C.

He		O <sub>2</sub>	
$P_i = 1.0 \text{ atm}$	$P_f = P_{He}$	$P_i = 1.0 \text{ atm}$	$P_f = P_{O_2}$
$V_i = 46 \text{ L}$	$V_f = 5.0 \text{ L}$	$V_i = 12 \text{ L}$	$V_f = 5.0 \text{ L}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

137

---

---

---

---

---

---

---

---

## Ex. Solution (cont)

- First calculate pressure of each gas in 5 L tank ( $P_f$ ) using combined gas law

$$P_{He} = \frac{P_i V_i}{V_f} = \frac{1 \text{ atm} \times 46 \text{ L}}{5 \text{ L}} = 9.2 \text{ atm}$$

$$P_{O_2} = \frac{P_i V_i}{V_f} = \frac{1 \text{ atm} \times 12 \text{ L}}{5 \text{ L}} = 2.4 \text{ atm}$$

- Then use these partial pressures to calculate total pressure

$$P_{total} = P_{He} + P_{O_2} = 9.2 \text{ atm} + 2.4 \text{ atm} = 11.6 \text{ atm}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

138

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** 250 mL of methane,  $\text{CH}_4$ , at 35 °C and 0.55 atm and 750 mL of propane,  $\text{C}_3\text{H}_8$ , at 35 °C and 1.5 atm, were introduced into a 10.0 L container. What is the final pressure, in torr, of the mixture?

- A. 95.6 torr
- B.  $6.20 \times 10^4$  torr
- C.  $3.4 \times 10^3$  torr
- D. 760 torr
- E. 59.8 torr

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

139

---

---

---

---

---

---

---

---

## Your Turn! - Solution

$$P(\text{CH}_4) = \frac{0.55 \text{ atm} \times 0.250 \text{ L}}{10.0 \text{ L}} = 0.0138 \text{ atm}$$

$$P(\text{C}_3\text{H}_8) = \frac{1.5 \text{ atm} \times 0.750 \text{ L}}{10.0 \text{ L}} = 0.112 \text{ atm}$$

$$P_T = (0.0138 + 0.112) \text{ atm} \times \frac{760 \text{ torr}}{\text{atm}} = 95.6 \text{ torr}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

140

---

---

---

---

---

---

---

---

## Mole Fractions and Mole Percents

### Mole Fraction

- Ratio of number moles of given component in mixture to total number moles in mixture

$$X_A = \frac{n_A}{n_A + n_B + n_C + \cdots + n_Z} = \frac{n_A}{n_{\text{total}}}$$

$$n_A = P_A \left( \frac{V}{RT} \right)$$

$$X_A = \frac{P_A}{P_{\text{total}}} = \frac{n_A}{n_{\text{total}}}$$

$$P_A = X_A \times P_{\text{total}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

141

---

---

---

---

---

---

---

---

- **Ex.** The partial pressure of oxygen was observed to be 156 *torr* in air with a total atmospheric pressure of 743 *torr*. Calculate the mole fraction of O<sub>2</sub> present

$$X_A = \frac{P_A}{P_{total}}$$

$$X_{O_2} = \frac{156\text{torr}}{743\text{torr}} = 0.210$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

142

---

---

---

---

---

---

---

- **Ex.** The mole fraction of nitrogen in the air is 0.7808. Calculate the partial pressure of N<sub>2</sub> in air when the atmospheric pressure is 760. *torr*.

$$P_{N_2} = X_{N_2} \times P_{total}$$

$$P_{N_2} = 0.7808 \times 760\text{torr} = 593\text{torr}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

143

---

---

---

---

---

---

---

### Your Turn!

- Ex.** 250 mL of methane, CH<sub>4</sub>, at 35 °C and 0.55 atm and 750 mL of propane, C<sub>3</sub>H<sub>8</sub>, at 35 °C and 1.5 atm were introduced into a 10.0 L container. What is the mole fraction of methane in the mixture?

- A. 0.50
- B. 0.11
- C. 0.89
- D. 0.25
- E. 0.33

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

144

---

---

---

---

---

---

---



## Your Turn! - Solution

$$P(\text{CH}_4) = \frac{0.55 \text{ atm} \times 0.250 \text{ L}}{10.0 \text{ L}} = 0.0138 \text{ atm}$$

$$P(\text{C}_3\text{H}_8) = \frac{1.5 \text{ atm} \times 0.750 \text{ L}}{10.0 \text{ L}} = 0.112 \text{ atm}$$

$$X_{\text{CH}_4} = \frac{0.0138 \text{ atm}}{(0.0138 + 0.112) \text{ atm}} = 0.110$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

145

---

---

---

---

---

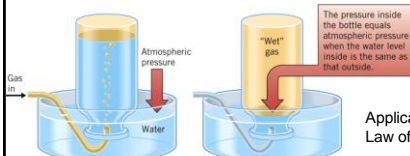
---

---

---

## Collecting Gases over Water

- Water vapor is present because molecules of water escape from surface of liquid and collect in space above liquid
- Molecules of water return to liquid
  - rate of escape = rate of return**
- Number of water molecules in vapor state remains constant
- Gas saturated with water vapor = "Wet" gas



Application of Dalton's Law of Partial Pressures

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

146

---

---

---

---

---

---

---

---

## Vapor Pressure

- Pressure exerted by vapor present in space above any liquid
  - Constant at constant T
- When wet gas collected over water, we usually want to know how much "dry" gas this corresponds to
  - $P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$**
  - Rearranging
  - $P_{\text{gas}} = P_{\text{total}} - P_{\text{water}}$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

147

---

---

---

---

---

---

---

---

**Ex.** A sample of oxygen is collected over water at 20.0 °C and a pressure of 738 torr. Its volume is 310 mL. The vapor pressure of water at 20°C is 17.54 torr.

- What is the partial pressure of O<sub>2</sub>?
- What would the volume be when dry at STP?

**a.**  $P_{O_2} = P_{total} - P_{water}$   
 $= 738 \text{ torr} - 17.5 \text{ torr} = \mathbf{720 \text{ torr}}$

---

---

---

---

---

---

---

---

### Ex. Solution

- b.** calculate  $P_{O_2}$  at STP

$$P_1 = 720 \text{ torr} \quad P_2 = 760 \text{ torr}$$

$$V_1 = 310 \text{ mL} \quad V_2 = ?$$

$$T_1 = 20.0 + 273.12 = 293 \text{ K}$$

$$T_2 = 0.0 + 273 \text{ K} = 273 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

$$V_2 = \frac{720 \text{ torr} \times 310 \text{ mL} \times 273 \text{ K}}{293 \text{ K} \times 760 \text{ torr}} \quad V_2 = \mathbf{274 \text{ mL}}$$

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** An unknown gas was collected by water displacement. The following data was recorded:  
 T = 27.0 °C; P = 750 torr; V = 37.5 mL; Gas mass = 0.0873 g;  $P^{vap}(H_2O) = 26.98 \text{ torr}$

Determine the molecular weight of the gas.

- 5.42 g/mol
- 30.2 g/mol
- 60.3 g/mol
- 58.1 g/mol
- 5.81 g/mol

---

---

---

---

---

---

---

---

## Your Turn! - Solution

$$MW = \frac{gRT}{PV} = \frac{0.0873 \text{ g} \times 0.0821 \frac{\text{L atm}}{\text{K mol}} \times 300 \text{ K}}{(750 - 26.98) \text{ torr} \times 0.0375 \text{ L}}$$

$$MW = 60.3 \text{ g/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

151

---

---

---

---

---

---

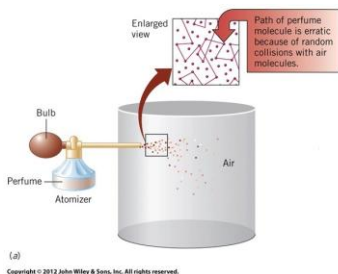
---

---

## Diffusion

- Complete spreading out and intermingling of molecules of one gas into and among those of another gas

- Ex.** Perfume in room



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

152

---

---

---

---

---

---

---

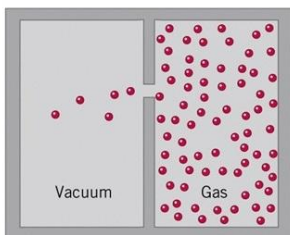
---

## Effusion

- Movement of gas molecules
- Through extremely small opening into vacuum

### Vacuum

- No other gases present in other half



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

153

---

---

---

---

---

---

---

---

## Graham's Law of Effusion

- Rates of effusion of gases are inversely proportional to square roots of their densities,  $d$ , when compared at identical pressures and temperatures

$$\text{Effusion Rate} \propto \frac{1}{\sqrt{d}} \quad (\text{constant } P \text{ and } T)$$

$$\frac{\text{Effusion Rate (A)}}{\text{Effusion Rate (B)}} = \frac{\sqrt{d_B}}{\sqrt{d_A}} = \sqrt{\frac{d_B}{d_A}}$$

$$\frac{\text{Effusion Rate (A)}}{\text{Effusion Rate (B)}} = \frac{\sqrt{d_B}}{\sqrt{d_A}} = \sqrt{\frac{M_B}{M_A}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

154

---

---

---

---

---

---

---

---

## Graham's Law of Effusion

**Ex.** Calculate the ratio of the effusion rates of hydrogen gas ( $\text{H}_2$ ) and uranium hexafluoride ( $\text{UF}_6$ ) - a gas used in the enrichment process to produce fuel for nuclear reactors.

- First must compute MM's
  - MM ( $\text{H}_2$ ) = 2.016 g/mol
  - MM ( $\text{UF}_6$ ) = 352.02 g/mol

$$\frac{\text{Effusion Rate (H}_2\text{)}}{\text{Effusion Rate (UF}_6\text{)}} = \sqrt{\frac{M_{\text{UF}_6}}{M_{\text{H}_2}}} = \sqrt{\frac{352.02}{2.016}} = 13.2$$

- Thus the very light  $\text{H}_2$  molecules effuse ~13 times as fast as the massive  $\text{UF}_6$  molecules.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

155

---

---

---

---

---

---

---

---

- Ex.** For the series of gases He, Ne, Ar,  $\text{H}_2$ , and  $\text{O}_2$  what is the order of increasing rate of effusion?

substance	He	Ne	Ar	$\text{H}_2$	$\text{O}_2$
MM	4	20	40	2	32

- Lightest are fastest
- So  $\text{H}_2 > \text{He} > \text{Ne} > \text{O}_2 > \text{Ar}$

**Heavier gases effuse more slowly**  
**Lighter gases effuse more rapidly**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

156

---

---

---

---

---

---

---

---

## Postulates of Kinetic Theory of Gases

1. Particles are so small compared with distances between them, so volume of individual particles can be assumed to be negligible.
  - $V_{\text{gas}} \sim 0$
2. Particles are in constant motion
  - Collisions of particles with walls of container are cause of pressure exerted by gas
  - number collisions  $\propto P_{\text{gas}}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

157

## Postulates of Kinetic Theory of Gases

3. Particles are assumed to exert no force on each other
  - Assumed neither to attract nor to repel each other
4. Average kinetic energy of collection of gas particles is assumed to be directly proportional to Kelvin Temperature
  - $KE_{\text{avg}} \propto T_K$

Root-mean-square speed  $v_{\text{rms}} = \sqrt{\frac{3RT}{M_m}}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

158

Ex: What are the rms speeds of helium atoms, and nitrogen, hydrogen, and oxygen molecules at 25 °C?

$T = 25\text{ °C} + 273 = 298\text{ K}$ .  $R = 8.314\text{ J/mol K}$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M_m}}$$

Element	Mass (kg)	rms speed (m/s)
He	$6.64 \times 10^{-27}$	1360
H <sub>2</sub>	$3.32 \times 10^{-27}$	1930
N <sub>2</sub>	$4.64 \times 10^{-26}$	515
O <sub>2</sub>	$5.32 \times 10^{-26}$	482

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

159

## Kinetic Theory of Gases

- This means  $T \propto KE_{ave}$
- Specifically
- As increase  $T$ ,  $\uparrow KE_{ave}$ 
  - $\uparrow$  number collisions with walls, thereby increasing  $P$
  - Kinetic energy For 1 mole of gas is:

$$KE_{ave} = \frac{3}{2}RT$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

160

---

---

---

---

---

---

---

---

## Real Gases

- Have *finite* volumes
- **Do** exert forces on each other
- Real Gases deviate **Why?**

$$\frac{PV}{T} = \text{constant}$$

$$\frac{PV}{nT} = R$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

161

---

---

---

---

---

---

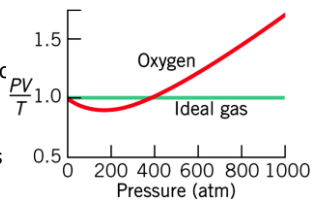
---

---

## Real Gases Deviate from Ideal Gas Law

1. Gas molecules have finite  $V$ 's

- $\therefore$  Take up space
- Less space of kinetic motions
- $V_{motions} < V_{container}$
- $\therefore$  particles hit walls of container more often
- $\uparrow P$  over ideal



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

162

---

---

---

---

---

---

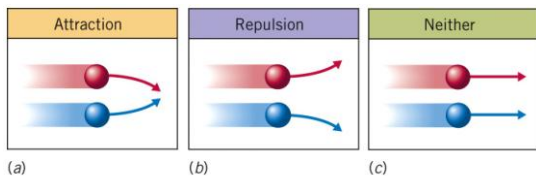
---

---

## Real Gases

### 2. Particles DO attract each other

- Even weak attractions means they hit walls of container less often
- $\therefore \downarrow P$  over ideal gas



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

163

---

---

---

---

---

---

---

---

## van der Waal's equation for Real Gases

$$\underbrace{\left( P + \frac{n^2 a}{V^2} \right)}_{\text{corrected } P} * \underbrace{(V - nb)}_{\text{corrected } V} = nRT$$

- **a** and **b** are **van der Waal's** constants
- Obtained by measuring **P, V, and T** for real gases over wide range of conditions

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

164

---

---

---

---

---

---

---

---

## van der Waal's equation for Real Gases

$$\underbrace{\left( P + \frac{n^2 a}{V^2} \right)}_{\text{corrected } P} * (V - nb) = nRT$$

- **a** — Pressure correction
  - Indicates some **attractions** between molecules
  - Large **a**
    - Means strong attractive forces between molecules
  - Small **a**
    - Means weak attractive forces between molecules

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

165

---

---

---

---

---

---

---

---

## van der Waal's equation for Real Gases

$$\left(P + \frac{n^2 a}{V^2}\right) * \underbrace{(V - nb)}_{\text{corrected V}} = nRT$$

- **b** — Volume correction
  - Deals with **sizes** of molecules
  - Large **b**
    - Means large molecules
  - Small **b**
    - Means small molecules
- Gases that are most easily liquefied have largest van der Waal's constants

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

166

Ex: When will a real gas behave most like an ideal gas?

- A) at high temperatures and high pressures
- B) at low temperatures and high pressures
- C) at low temperatures and low pressures
- D) at high temperatures and low pressures

TABLE 10.3 • van der Waals Constants for Gas Molecules

Substance	$a$ (L <sup>2</sup> ·atm/mol <sup>2</sup> )	$b$ (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H <sub>2</sub>	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
Cl <sub>2</sub>	6.49	0.0562
H <sub>2</sub> O	5.46	0.0305
CH <sub>4</sub>	2.25	0.0428
CO <sub>2</sub>	3.59	0.0427
CCl <sub>4</sub>	20.4	0.1383

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

Ex: If 1.000 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 1.000 atm. Use the van der Waals equation and the constants in Table 10.3 to estimate the pressure exerted by 1.000 mol of Cl<sub>2</sub>(g) in 22.41 L at 0.0 °C.

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

**Solve:** Substituting  $n = 1.000$  mol,  $R = 0.08206$  L·atm/mol·K,  $T = 273.2$  K,  $V = 22.41$  L,  $a = 6.49$  L<sup>2</sup>·atm/mol<sup>2</sup>, and  $b = 0.0562$  L/mol:

$$P = \frac{(1.000 \text{ mol})(0.08206 \text{ L·atm/mol·K})(273.2 \text{ K})}{22.41 \text{ L} - (1.000 \text{ mol})(0.0562 \text{ L/mol})} - \frac{(1.000 \text{ mol})^2(6.49 \text{ L}^2\text{·atm/mol}^2)}{(22.41 \text{ L})^2}$$

$$= 1.003 \text{ atm} - 0.013 \text{ atm} = 0.990 \text{ atm}$$

Ex.2. Use Van de Waal's equation to calculate the pressure exerted by 1.00 mol Cl<sub>2</sub> confined to a volume of 2.00 L at 273K. The value of  $a=6.49$  L<sup>2</sup> atm/mol<sup>2</sup> and  $b=0.0562$  L/mol

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

168



## Chapter 3

### Energy and Chemical Change Thermodynamics

**Chemistry: The Molecular Nature  
of Matter, 6E**

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

### Thermochemistry

- Study of energies given off by or absorbed by reactions.

#### Thermodynamics

- Study of energy transfer (flow)

#### Energy (E)

- Ability to do work or to transfer heat.

#### Kinetic Energy (KE)

- Energy of motion
- $KE = \frac{1}{2}mv^2$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

170

---

---

---

---

---

---

---

### Potential Energy (PE)

- Stored energy
- Exists in natural attractions and repulsions
  - Gravity
  - Positive and negative charges
  - Springs



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved. Photo Credits Images

#### Chemical Energy

- PE possessed by chemicals
- Stored in chemical bonds
- Breaking bonds requires energy
- Forming bonds releases energy

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

171

---

---

---

---

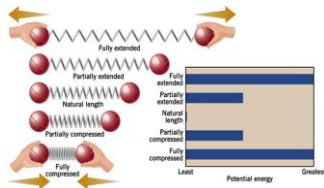
---

---

---

## Law of Conservation of Energy

- Energy can neither be created nor destroyed
- Can only be converted from one form to another
- Total Energy of universe is constant



$$\text{Total Energy} = \text{Potential Energy} + \text{Kinetic Energy}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

172

---

---

---

---

---

---

---

---

## Temperature vs. Heat

### Temperature

- Proportional to **average** kinetic energy of object's particles
- Higher average kinetic energy means
  - Higher temperature
  - Faster moving molecules

### Heat

- Energy transferred between objects
- Caused by temperature difference
- Always passes spontaneously from warmer objects to colder objects
- Transfers until both are the same temperature

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

173

---

---

---

---

---

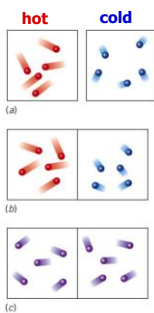
---

---

---

## Heat Transfer

- Hot and cold objects placed in contact
  - Molecules in hot object moving faster
- KE transfers from hotter to colder object
  - ↓ average KE of hotter object
  - ↑ average KE of colder object
- Over time
  - Average KEs of both objects becomes the same
  - Temperature of both becomes the same



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

174

---

---

---

---

---

---

---

---

## Units of Energy

### Joule (J)

$$1\text{J} = \frac{1\text{ kg} \cdot \text{m}^2}{\text{s}^2}$$

- value is greater than 1000 J, use kJ
- 1 kJ = 1000 J

### calorie (cal)

Energy needed to raise T of 1 g H<sub>2</sub>O by 1 °C

$$1\text{ cal} = 4.184\text{ J} \quad (\text{exactly})$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

175

---

---

---

---

---

---

---

## Internal Energy (E)

- Sum of energies of all particles in system

$E$  = Total energy of system

$E$  = Potential + Kinetic =  $PE + KE$

### Change in Internal Energy

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- $\Delta$  means change
- final – initial
- What we can actually measure
- Want to know change in  $E$  associated with given process

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

176

---

---

---

---

---

---

---

## $\Delta E$ , Change in Internal Energy

- For reaction: **reactants**  $\longrightarrow$  **products**
  - $\Delta E = E_{\text{products}} - E_{\text{reactants}}$ 
    - Can use to do something useful
      - Work
      - Heat
  - If system absorbs energy during reaction
    - Energy coming into system is positive (+)
    - Final energy > initial energy
- Ex.** Photosynthesis *or* charging battery
- As system absorbs energy
    - Increase potential energy
    - Available for later use

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

177

---

---

---

---

---

---

---

## $\Delta E$ , Change in Internal Energy

- $\Delta E = E_{\text{products}} - E_{\text{reactants}}$ 
  - Energy change can appear entirely as heat
  - Can measure heat
  - Can't measure  $E_{\text{product}}$  or  $E_{\text{reactant}}$
  - Fortunately, we are more interested in  $\Delta E$
  - Energy of system depends only on its current condition
    - DOES NOT depend on:
      - How system got it
      - What E for system might be sometime in future

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

178

---

---

---

---

---

---

---

## State Functions

- Any property that **only** depends on object's current state or condition
- Independence from method, path or mechanism by which change occurs is important feature of all state functions
- Some State functions:
  - Internal energy  $\Delta E = E_f - E_i$
  - Pressure  $\Delta P = P_f - P_i$
  - Temperature  $\Delta t = t_f - t_i$
  - Volume  $\Delta V = V_f - V_i$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

179

---

---

---

---

---

---

---

## Defining the System

### System

- What we are interested in studying
  - Reaction in beaker

### Surroundings

- Everything else
  - Room in which reaction is run

### Boundary

- Separation between system and surroundings
  - Visible **Ex.** Walls of beaker
  - Invisible **Ex.** Line separating warm and cold fronts

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

180

---

---

---

---

---

---

---

## Three Types of Systems

### Open System

- Open to atmosphere
- Gain or lose mass and energy across boundary
- Most reactions done in open systems



### Closed System

- Not open to atmosphere
- Energy can cross boundary, but mass **cannot**



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

181

---

---

---

---

---

---

---

## Three Types of Systems

### Isolated System

- No energy or matter can cross boundary
  - Energy and mass are constant
- Ex.** Thermos bottle



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

182

---

---

---

---

---

---

---

## Your Turn!

**Ex.** A closed system can \_\_\_\_\_

- A. include the surroundings.
- B. absorb energy and mass.
- C. not change its temperature.
- D. not absorb or lose energy and mass.
- E. absorb or lose energy, but not mass.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

183

---

---

---

---

---

---

---

## Heat ( $q$ )

- Can't measure heat directly
- Heat ( $q$ ) gained or lost by an object
  - Directly proportional to temperature change ( $\Delta t$ ) it undergoes.  $\Delta t = t - t$
  - Adding heat, increases temperature  $\Delta t > 0$ ,  $q > 0$
  - Removing heat, decreases temperature  $\Delta t < 0$ ,  $q < 0$
- Measure changes in temperature to quantify amount of heat transferred

$$q = C \times \Delta t$$

- $C$  = heat capacity

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

184

---

---

---

---

---

---

---

## Heat Capacity ( $C$ )

- Amount of heat ( $q$ ) required to raise temperature of object by 1 °C

$$\text{Heat Exchanged} = \text{Heat Capacity} \times \Delta t$$

$$q = C \times \Delta t$$

- **Units** =  $J/^\circ C$  or  $J \cdot ^\circ C^{-1}$

Depends on two factors

1. Sample size or amount (mass)
  - Doubling amount doubles heat capacity
2. Identity of substance
  - Water vs. iron

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

185

---

---

---

---

---

---

---

## Learning Check: Heat Capacity

**Ex.** A cup of water is used in an experiment. Its heat capacity is known to be 720 J/ °C. How much heat will it absorb if the experimental temperature changed from 19.2 °C to 23.5 °C?

$$q = C \times \Delta t$$

$$q = 720 \frac{J}{^\circ C} \times (23.5 - 19.2^\circ C)$$

$$q = 720 \frac{J}{^\circ C} \times (4.3^\circ C)$$

$$q = 3.1 \times 10^3 J$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

186

---

---

---

---

---

---

---

## Learning Check: Heat Capacity

**Ex.** If it requires 4.184 J to raise the temperature of 1.00 g of water by 1.00 °C, calculate the heat capacity of 1.00 g of water.

$$C = \frac{q}{\Delta t}$$

$$C_{1.00 \text{ g}} = \frac{4.184 \text{ J}}{1.00 \text{ }^{\circ}\text{C}} = \mathbf{4.18 \text{ J/}^{\circ}\text{C}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

187

---

---

---

---

---

---

---

## Your Turn!

**Ex.** What is the heat capacity of 300 g of water if it requires 2510 J to raise the temperature of the water by 2.00 °C?

A. 4.18 J/°C

B. 418 J/°C

C. 837 J/°C

D.  $1.26 \times 10^3$  J/°C

E.  $2.51 \times 10^3$  J/°C

$$C_{300 \text{ g}} = \frac{2510 \text{ J}}{2.00 \text{ }^{\circ}\text{C}} =$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

188

---

---

---

---

---

---

---

## Specific Heat (*s*)

- Amount of Heat Energy needed to raise T of 1 g substance by 1 °C

$$C = s \times m \quad \text{or} \quad s = \frac{C}{m}$$

- Units**

- $\text{J}/(\text{g}\cdot^{\circ}\text{C})$  or  $\text{J g}^{-1}\text{ }^{\circ}\text{C}^{-1}$
- Unique to each substance
- Large specific heat means substance releases large amount of heat as it cools

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

189

---

---

---

---

---

---

---

## Learning Check

**Ex.** Calculate the specific heat of water if the heat capacity of 100 g of water is 418 J/°C.

$$s = \frac{C}{m} \quad s = \frac{418 \text{ J/}^\circ\text{C}}{100. \text{ g}} = \mathbf{4.18 \text{ J/(g}\cdot^\circ\text{C)}}$$

- What is the specific heat of water if heat capacity of 1.00 g of water is 4.18 J/°C?

$$s = \frac{4.18 \text{ J/}^\circ\text{C}}{1.00 \text{ g}} = \mathbf{4.18 \text{ J/(g}\cdot^\circ\text{C)}}$$

- Thus, **heat capacity is independent of amount**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

190

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** The specific heat of silver 0.235 J g<sup>-1</sup> °C<sup>-1</sup>. What is the heat capacity of a 100. g sample of silver?

$$C = s \times m$$

A. 0.235 J/°C

B. 2.35 J/°C

C. 23.5 J/°C

D. 235 J/°C

E. 2.35 × 10<sup>3</sup> J/°C

$$C = 0.235 \frac{\text{J}}{\text{g}\cdot^\circ\text{C}} \times 100. \text{ g}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

191

---

---

---

---

---

---

---

---

Table 7.1 Specific Heats

Substance	Specific Heat, J g <sup>-1</sup> °C <sup>-1</sup> (25 °C)
Carbon (graphite)	0.711
Copper	0.387
Ethyl alcohol	2.45
Gold	0.129
Granite	0.803
Iron	0.4498
Lead	0.128
Olive oil	2.0
Silver	0.235
Water (liquid)	4.184

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

192

---

---

---

---

---

---

---

---



## Using Specific Heat

Heat Exchanged = (Specific Heat  $\times$  mass)  
 $\times \Delta t$

$$q = s \times m \times \Delta t$$

Units =  $\text{J}/(\text{g} \times ^\circ\text{C}) \times \text{g} \times ^\circ\text{C} = \text{J}$

- Substances with high specific heats resist  $\Delta T$  changes
- Makes it difficult to change temperature widely
- Water has unusually high specific heat

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

193

---

---

---

---

---

---

---

## Learning Check: Specific Heat

**Ex.** Calculate the specific heat of a metal if it takes 235 J to raise the temperature of a 32.91 g sample by  $2.53^\circ\text{C}$ .

$$q = m \times s \times \Delta t$$

$$s = \frac{q}{m \times \Delta t} = \frac{235\text{J}}{32.91\text{g} \times 2.53^\circ\text{C}}$$

$$s = 2.82 \frac{\text{J}}{\text{g}^\circ\text{C}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

194

---

---

---

---

---

---

---

## Ex. 1 Using Specific Heat

**Ex.** If a 38.6 g of gold absorbs 297 J of heat, what will the final temperature if the initial temperature is  $24.5^\circ\text{C}$ ? The specific heat of gold is  $0.129 \text{ J g}^{-1} ^\circ\text{C}^{-1}$ .

Need to find  $t_{\text{final}}$

$$\Delta t = t_f - t_i$$

First use  $q = s \times m \times \Delta t$  to calculate  $\Delta t$

$$\Delta t = \frac{q}{s \cdot m} = \frac{297\text{J}}{0.129\text{J} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1} \times 38.6\text{g}} = 59.6^\circ\text{C}$$

$$59.6^\circ\text{C} = t_f - 24.5^\circ\text{C}$$

$$t_f = 59.6^\circ\text{C} + 24.5^\circ\text{C}$$

$$= 84.1^\circ\text{C}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

195

---

---

---

---

---

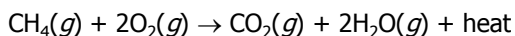
---

---

## Exothermic Reaction

- Reaction where products have less chemical energy than reactants
- Some chemical energy converted to kinetic energy
- Reaction releases heat to surroundings
- Heat leaves the system;  $q$  negative ( - )
- Reaction gets warmer ( $\uparrow T$ )

**Ex.**



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

196

---

---

---

---

---

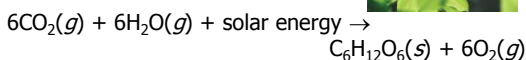
---

---

## Endothermic Reaction

- Reaction where products have more chemical energy than reactants
- Some kinetic energy converted to chemical energy
- Reaction absorbs heat from surroundings
- Heat added to system;  $q$  positive ( + )
- Reaction becomes colder ( $T \downarrow$ )

**Ex.** Photosynthesis



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

197

---

---

---

---

---

---

---

## Work Convention

$$\text{Work} = -P \times \Delta V$$

- **P** = opposing pressure against which piston pushes
- **$\Delta V$**  = change in volume of gas during expansion
- **$\Delta V = V_{\text{final}} - V_{\text{initial}}$**
- For Expansion
  - Since  $V_{\text{final}} > V_{\text{initial}}$
  - **$\Delta V$**  must be positive
  - So **expansion** work is negative  **$\Delta V > 0$**
  - Work done **by** system on surrounding,  **$W < 0$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

198

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Calculate the work associated with the expansion of a gas from 152.0 L to 189.0 L at a constant pressure of 17.0 atm.

A. 629 L atm

$$\text{Work} = -P \times \Delta V$$

B. -629 L atm

$$\Delta V = 189.0 \text{ L} - 152.0 \text{ L}$$

C. -315 L atm

$$w = -17.0 \text{ atm} \times 37.0 \text{ L}$$

D. 171 L atm

E. 315 L atm

## First Law of Thermodynamics

- "Energy of system may be transferred as heat or work, but not lost or gained."
- If we monitor heat transfers ( $q$ ) of all materials involved and all work processes, can predict that their sum will be zero
  - Some materials gain (have +) energy
  - Others lose (have -) energy
- By monitoring surroundings, we can predict what is happening to system

## Two Methods of *Energy* Exchange Between System and Surroundings

Heat  $q$                       Work  $w$

$$\Delta E = q + w$$

- Conventions of heat and work

$q$	+	Heat <b>absorbed</b> by system	$E_{\text{system}} \uparrow$
$q$	-	Heat <b>released</b> by system	$E_{\text{system}} \downarrow$
$w$	+	Work done <b>on</b> system	$E_{\text{system}} \uparrow$
$w$	-	Work done <b>by</b> system	$E_{\text{system}} \downarrow$

## Heat and Work

Two ways system can exchange internal energy with surroundings

### 1. Heat

- Heat absorbed, System's  $q \uparrow$
- Heat lost, System's  $q \downarrow$

### 2. Work

- Is exchanged when pushing force moves something through distance

**Ex.** Compression of system's gas  $W > 0$   
expansion of system's gas  $W < 0$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

202

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** A gas **releases** 3.0 J of heat and then **performs** 12.2 J of work. What is the change in internal energy of the gas?

A. -15.2 J

$$\Delta E = q + w$$

B. 15.2 J

$$\Delta E = -3.0 \text{ J} + (-12.2 \text{ J})$$

C. -9.2 J

D. 9.2 J

E. 3.0 J

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

203

---

---

---

---

---

---

---

---

## Heat at Constant Pressure ( $q_p$ )

- Chemists usually do NOT run reactions at constant  $V$
- Usually do reactions in open containers
  - Open to atmosphere; constant  $P$
  - Heat of reaction at constant Pressure ( $q_p$ )
- $\Delta E = q_p + w = q_p - P\Delta V$
- $q_p = \Delta E + P\Delta V$   
 $H$  = state function
- At constant Pressure:  $\Delta H = q_p$   
 $\Delta H = \Delta E + P\Delta V$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

204

---

---

---

---

---

---

---

---

## Enthalpy Change ( $\Delta H$ )

$\Delta H$  = state function

- $\Delta H = H_{\text{final}} - H_{\text{initial}}$
- $\Delta H = H_{\text{products}} - H_{\text{reactants}}$
- Significance of sign of  $\Delta H$

### Endothermic reaction

- System absorbs energy from surroundings
- $\Delta H > 0$  positive

### Exothermic reaction

- System loses energy to surroundings
- $\Delta H < 0$  negative

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

205

---

---

---

---

---

---

---

## Enthalpy vs. Internal Energy

- $\Delta H = \Delta E + P\Delta V$

Rearranging gives

- $\Delta H - \Delta E = P\Delta V$

- Difference between  $\Delta H$  and  $\Delta E$  is  $P\Delta V$
- Reactions where form or consume **gases**
  - $P\Delta V$  can be large
- Reactions involving only liquids and solids
  - $\Delta V$  negligible  $\Delta V \approx 0$
  - So  $\Delta H \approx \Delta E$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

206

---

---

---

---

---

---

---

## Enthalpy Changes in Chemical Reactions

- Focus on systems
- Endothermic
  - Reactants + **heat**  $\longrightarrow$  products
- Exothermic
  - Reactants  $\longrightarrow$  products + **heat**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

207

---

---

---

---

---

---

---

## $\Delta H$ in Chemical Reactions

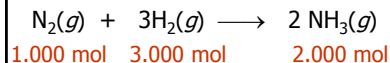
### Standard Conditions for $\Delta H^\circ$

- 25 °C and 1 atm

### Standard Heat of Reaction ( $\Delta H^\circ$ )

- Enthalpy change for reaction at 1 atm and 25 °C

#### Ex.



- When  $\text{N}_2$  and  $\text{H}_2$  react to form  $\text{NH}_3$  at 25 °C and 1 atm
- 92.38 kJ released
- $\Delta H^\circ = -92.38 \text{ kJ}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

208

---

---

---

---

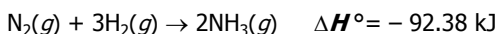
---

---

---

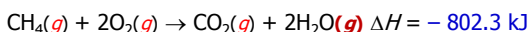
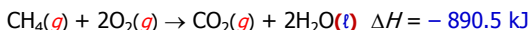
## Thermochemical Equation

- Write  $\Delta H^\circ$  immediately after equation



- Must give physical states of products and reactants**

- $\Delta H_{\text{rxn}}$  different for different states



- Difference = energy to vaporize water

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

209

---

---

---

---

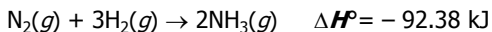
---

---

---

## Thermochemical Equation

- Write  $\Delta H^\circ$  immediately after equation



- coefficients = # moles**

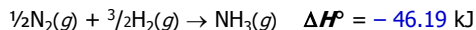
- 92.38 kJ released  $\leftrightarrow$  2 moles of  $\text{NH}_3$  formed

- If 10 mole of  $\text{NH}_3$  formed



- $\Delta H_{\text{rxn}} = (5 \times -92.38 \text{ kJ}) = -461.9 \text{ kJ}$

- Can have fractional coefficients



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

210

---

---

---

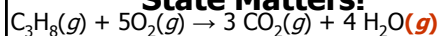
---

---

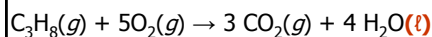
---

---

### State Matters!

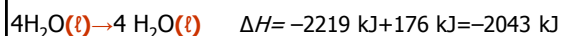
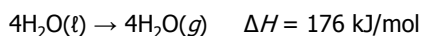
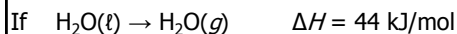


$$\Delta H = -2043 \text{ kJ}$$



$$\Delta H = -2219 \text{ kJ}$$

Note: there is difference in energy because states do not match



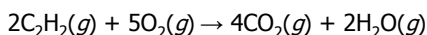
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

211

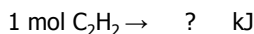
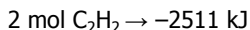
### Learning Check:

**Ex.** Consider the following reaction:



$$\Delta H = -2511 \text{ kJ}$$

How many kJ are released for 1 mol  $\text{C}_2\text{H}_2$ ?



$$\frac{-2511 \text{ kJ}}{2 \text{ mol } \text{C}_2\text{H}_2} \times 1 \text{ mol } \text{C}_2\text{H}_2 = \mathbf{-1,256 \text{ kJ}}$$

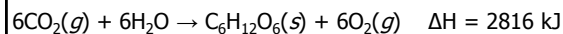
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

212

### Learning Check:

**EX.** Consider the reaction



A) how many kJ are required for 44 g  $\text{CO}_2$  (MM = 44.01 g/mol)?

$$44 \text{ g } \text{CO}_2 \times \frac{1 \text{ mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \times \frac{2816 \text{ kJ}}{6 \text{ mol } \text{CO}_2} = \mathbf{470 \text{ kJ}}$$

B) If 100. kJ are provided, what mass of  $\text{CO}_2$  can be converted to glucose?

$$100 \text{ kJ} \times \frac{6 \text{ mol } \text{CO}_2}{2816 \text{ kJ}} \times \frac{44.01 \text{ g } \text{CO}_2}{1 \text{ mol } \text{CO}_2} = \mathbf{9.38 \text{ g}}$$

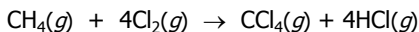
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

213

## Your Turn!

**Ex.** Based on the reaction



$$\Delta H = -434 \text{ kJ/mol CH}_4$$

What energy change occurs when 1.2 moles of methane reacts?

A.  $-3.6 \times 10^2 \text{ kJ}$        $\Delta H = -434 \text{ kJ/mol} \times 1.2 \text{ mol}$

B.  $+5.2 \times 10^2 \text{ kJ}$        $\Delta H = -520.8 \text{ kJ}$

C.  $-4.3 \times 10^2 \text{ kJ}$

D.  $+3.6 \times 10^2 \text{ kJ}$

E.  $-5.2 \times 10^2 \text{ kJ}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

214

---

---

---

---

---

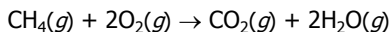
---

---

---

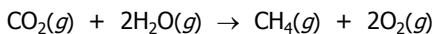
## Running Thermochemical Equations in Reverse

Consider the reaction



$$\Delta H^\circ = -802.3 \text{ kJ}$$

- Reverse thermochemical equation
- Must change sign of  $\Delta H$



$$\Delta H^\circ = +802.3 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

215

---

---

---

---

---

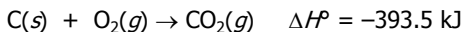
---

---

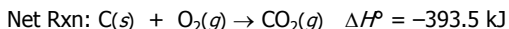
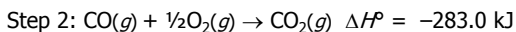
---

## Hess's Law Multiple Paths; Same $\Delta H^\circ$

**Path a: Single step**



**Path b: Two step**



- Chemically and thermochemically, identical results

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

216

---

---

---

---

---

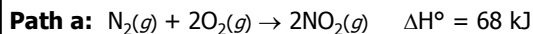
---

---

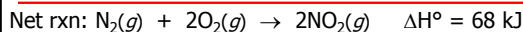
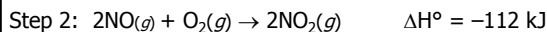
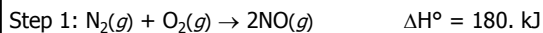
---



## Ex. Multiple Paths; Same $\Delta H^\circ$



**Path b:**



### Hess's Law of Heat Summation

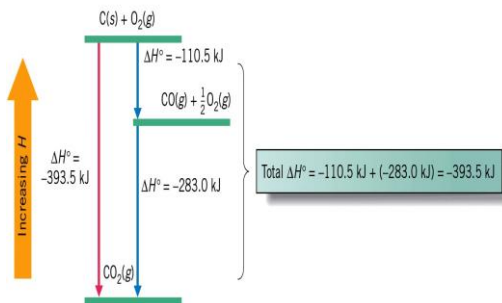
For any reaction that can be written into steps,  
value of  $\Delta H^\circ$  for reactions = sum of  $\Delta H^\circ$  values of  
each individual step

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

217

## Enthalpy Diagrams



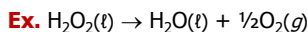
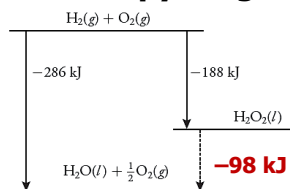
Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

218

## Enthalpy Diagrams



$$-286 \text{ kJ} = -188 \text{ kJ} + \Delta H_{\text{rxn}}$$

$$\Delta H_{\text{rxn}} = -286 \text{ kJ} - (-188 \text{ kJ})$$

$$\Delta H_{\text{rxn}} = -98 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

219

## Rules for Manipulating Thermochemical Equations

1. When equation is **reversed**, sign of  $\Delta H^\circ$  must also be **reversed** ( $-\Delta H^\circ$ ).
2. If all coefficients of equation are **multiplied or divided** by same factor, value of  $\Delta H^\circ$  must likewise be **multiplied or divided** by that factor
3. Formulas canceled from both sides of equation must be for substance in **same** physical states

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

220

---

---

---

---

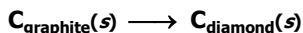
---

---

---

---

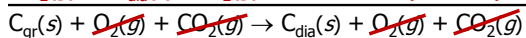
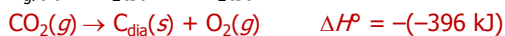
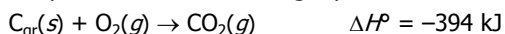
### Ex. Calculate $\Delta H^\circ$ for



Given  $\text{C}_{\text{gr}}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -394 \text{ kJ}$

**$-1 \times [\text{C}_{\text{dia}}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \quad \Delta H^\circ = -396 \text{ kJ}]$**

- To get desired equation, must reverse 2<sup>nd</sup> equation and add resulting equations



$$\Delta H^\circ = -394 \text{ kJ} + 396 \text{ kJ} = +2 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

221

---

---

---

---

---

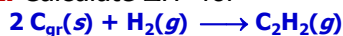
---

---

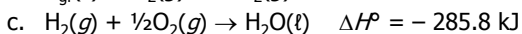
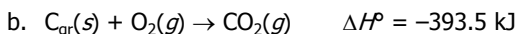
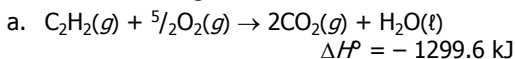
---

## Learning Check

**Ex.** Calculate  $\Delta H^\circ$  for



Given the following:



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

222

---

---

---

---

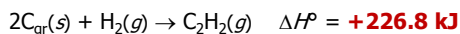
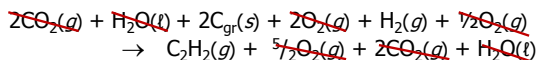
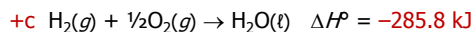
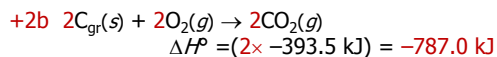
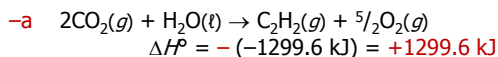
---

---

---

---

**Ex. Calculate for**  
 $2\text{C}_{\text{gr}}(\text{s}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_2(\text{g})$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

223

---

---

---

---

---

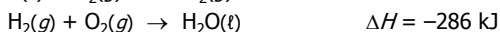
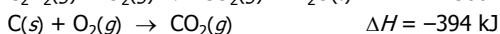
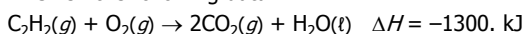
---

---

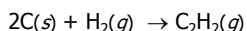
---

**Your Turn!**

**Ex.** Given the following data:



Calculate for the reaction



A. 226 kJ

B. -1980 kJ

C. -620 kJ  $\Delta H = +1300. \text{ kJ} + 2(-394 \text{ kJ}) + (-286 \text{ kJ})$

D. -226 kJ

E. 620 kJ

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

224

---

---

---

---

---

---

---

---

**Tabulating  $\Delta H^\circ$  values**

**Standard Enthalpy of Formation,  $\Delta H_f^\circ$**

- Amount of heat absorbed or evolved when one mole of substance is formed
- at 1 atm and 25 °C (298 K) from elements in their standard states
- Standard Heat of Formation  $\Delta H_f^\circ$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

225

---

---

---

---

---

---

---

---

## Standard State

- Most stable form and physical state of element at 1 atm and 25 °C (298 K)

element	Standard state
O	O <sub>2</sub> (g)
C	C <sub>gr</sub> (s)
H	H <sub>2</sub> (g)
Al	Al(s)
Ne	Ne(g)

Note: **All  $\Delta H_f^\circ$  of elements in their standard states = 0**

Forming element from itself.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

226

---

---

---

---

---

---

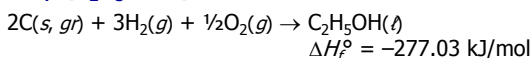
---

---

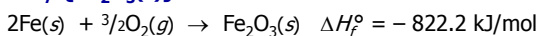
## Uses of Standard Enthalpy (Heat) of Formation, $\Delta H_f^\circ$

- From definition of  $\Delta H_f^\circ$ , can write balanced equations directly

$\Delta H_f^\circ\{\text{C}_2\text{H}_5\text{OH}(\ell)\}$



$\Delta H_f^\circ\{\text{Fe}_2\text{O}_3(\text{s})\}$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

227

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** What is the reaction that corresponds to the standard enthalpy of formation of  $\text{NaHCO}_3(\text{s})$ ,  $\Delta H_f^\circ = -947.7 \text{ kJ/mol}$ ?

- $\text{Na}(s) + \frac{1}{2}\text{H}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) + \text{C}(s, \text{gr}) \rightarrow \text{NaHCO}_3(\text{s})$
- $\text{Na}^+(\text{g}) + \text{H}^+(\text{g}) + 3\text{O}^{2-}(\text{g}) + \text{C}^{4+}(\text{g}) \rightarrow \text{NaHCO}_3(\text{s})$
- $\text{Na}^+(\text{aq}) + \text{H}^+(\text{aq}) + 3\text{O}^{2-}(\text{aq}) + \text{C}^{4+}(\text{aq}) \rightarrow \text{NaHCO}_3(\text{s})$
- $\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}(s) + \frac{1}{2}\text{H}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) + \text{C}(s, \text{gr})$
- $\text{Na}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{NaHCO}_3(\text{s})$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

228

---

---

---

---

---

---

---

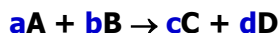
---

## Using $\Delta H_f^\circ$

2. Way to apply Hess's Law without needing to manipulate thermochemical equations

$$\Delta H_{\text{reaction}}^\circ = \left( \text{Sum of all } \Delta H_f^\circ \text{ of all of the products} \right) - \left( \text{Sum of all } \Delta H_f^\circ \text{ of all of the reactants} \right)$$

Consider the reaction:



$$\Delta H_{\text{reaction}}^\circ = c \times \Delta H_f^\circ(C) + d \times \Delta H_f^\circ(D) - \{a \times \Delta H_f^\circ(A) + b \times \Delta H_f^\circ(B)\}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

229

---

---

---

---

---

---

---

---

## Ex. Calculate $\Delta H_{\text{rxn}}^\circ$ Using $\Delta H_f^\circ$

Ex. Calculate  $\Delta H_{\text{rxn}}^\circ$  using  $\Delta H_f^\circ$  data for the reaction



1. Add  $\Delta H_f^\circ$  for each product times its coefficient

2. Subtract  $\Delta H_f^\circ$  for each reactant times its coefficient.

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{SO}_2(g)) + \frac{1}{2} \Delta H_f^\circ(\text{O}_2(g)) - \Delta H_f^\circ(\text{SO}_3(g))$$

$$\Delta H_{\text{rxn}}^\circ = -297 \text{ kJ/mol} + \frac{1}{2} (0 \text{ kJ/mol}) - (-396 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}}^\circ = 99 \text{ kJ/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

230

---

---

---

---

---

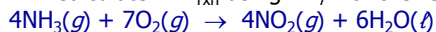
---

---

---

## Learning Check

Ex. Calculate  $\Delta H_{\text{rxn}}^\circ$  using  $\Delta H_f^\circ$  for the reaction



$$\Delta H_{\text{rxn}}^\circ = 4\Delta H_f^\circ(\text{NO}_2(g)) + 6\Delta H_f^\circ(\text{H}_2\text{O}(l)) - 4\Delta H_f^\circ(\text{NH}_3(g)) - 7\Delta H_f^\circ(\text{O}_2(g))$$

$$\Delta H_{\text{rxn}}^\circ = 4 \text{ mol}(34 \text{ kJ/mol}) + 6 \text{ mol}(-285.9 \text{ kJ/mol}) - 4 \text{ mol}(-46.0 \text{ kJ/mol}) - 7 \text{ mol}(0 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}}^\circ = [136 - 1715.4 + 184] \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = -1395 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

231

---

---

---

---

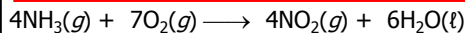
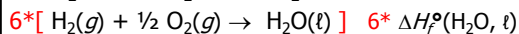
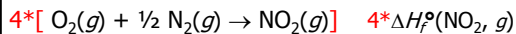
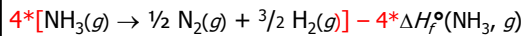
---

---

---

---

### Check Using Hess's Law



$$\Delta H_{\text{rxn}}^\circ = 4\Delta H_f^\circ(\text{NO}_2(g)) + 6\Delta H_f^\circ(\text{H}_2\text{O}(\ell))$$

$$- 4\Delta H_f^\circ(\text{NH}_3(g)) - 7\Delta H_f^\circ(\text{O}_2(g))$$

Same as before

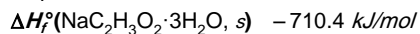
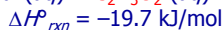
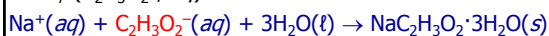
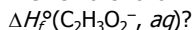
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

232

### Other Calculations

**Ex.** Given the following data, what is the value of



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

233

### Ex. cont.

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ(\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^\circ(\text{Na}^+, aq) - \Delta H_f^\circ(\text{C}_2\text{H}_3\text{O}_2^-, aq) - 3\Delta H_f^\circ(\text{H}_2\text{O}, \ell)$$

Rearranging

$$\Delta H_f^\circ(\text{C}_2\text{H}_3\text{O}_2^-, aq) = \Delta H_f^\circ(\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}, s) - \Delta H_f^\circ(\text{Na}^+, aq) - \Delta H_{\text{rxn}}^\circ - 3\Delta H_f^\circ(\text{H}_2\text{O}, \ell)$$

$$\Delta H_f^\circ(\text{C}_2\text{H}_3\text{O}_2^-, aq) = -710.4 \text{ kJ/mol} - (-239.7 \text{ kJ/mol}) - (-19.7 \text{ kJ/mol}) - 3(-285.9 \text{ kJ/mol})$$

$$= +406.7 \text{ kJ/mol}$$

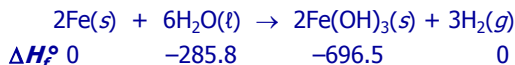
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

234

## Learning Check

**Ex.** Calculate  $\Delta H$  for this reaction using  $\Delta H_f^\circ$  data.



$$\Delta H_{\text{rxn}}^\circ = 2 * \Delta H_f^\circ(\text{Fe}(\text{OH})_3, s) + 3 * \Delta H_f^\circ(\text{H}_2, g) - 2 * \Delta H_f^\circ(\text{Fe}, s) - 6 * \Delta H_f^\circ(\text{H}_2\text{O}, l)$$

$$\Delta H_{\text{rxn}}^\circ = 2 \text{ mol} * (-696.5 \text{ kJ/mol}) + 3 * 0 - 2 * 0 - 6 \text{ mol} * (-285.8 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}}^\circ = -1393 \text{ kJ} + 1714.8 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = \mathbf{321.8 \text{ kJ}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

235

---

---

---

---

---

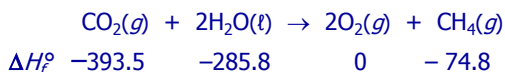
---

---

---

## Learning Check

**Ex.** Calculate  $\Delta H$  for this reaction using  $\Delta H_f^\circ$  data.



$$\Delta H_{\text{rxn}}^\circ = 2 * \Delta H_f^\circ(\text{O}_2, g) + \Delta H_f^\circ(\text{CH}_4, g) - \Delta H_f^\circ(\text{CO}_2, g) - 2 * \Delta H_f^\circ(\text{H}_2\text{O}, l)$$

$$\Delta H_{\text{rxn}}^\circ = 2 * 0 + 1 \text{ mol} * (-74.8 \text{ kJ/mol}) - 1 \text{ mol} * (-393.5 \text{ kJ/mol}) - 2 \text{ mol} * (-285.8 \text{ kJ/mol})$$

$$\Delta H_{\text{rxn}}^\circ = -74.8 \text{ kJ} + 393.5 \text{ kJ} + 571.6 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^\circ = \mathbf{890.3 \text{ kJ}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

236

---

---

---

---

---

---

---

---

## Converting Between $\Delta E$ and $\Delta H$ For Chemical Reactions

- When reaction occurs
  - $\Delta V$  caused by  $\Delta n$  of gas
- Not all reactants and products are gases
  - So redefine as  $\Delta n_{\text{gas}}$

Where  $\Delta n_{\text{gas}} = (n_{\text{gas}})_{\text{products}} - (n_{\text{gas}})_{\text{reactants}}$

- Substituting into

$$\Delta H = \Delta E + P\Delta V$$

- or

$$\Delta H = \Delta E + \Delta n_{\text{gas}} RT$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

237

---

---

---

---

---

---

---

---

**Ex.** Find  $\Delta E$  for the following reaction at 25 °C using data in Table 7.2?



**Step 1: Calculate  $\Delta H$  using  $\Delta H_f^\circ$  data (Table 7.2)**

Recall

$$\Delta H^\circ = (\Delta H_f^\circ)_{\text{products}} - (\Delta H_f^\circ)_{\text{reactants}}$$

$$\Delta H^\circ = 4\Delta H_f^\circ(\text{NO}_2) + \Delta H_f^\circ(\text{O}_2) - 2\Delta H_f^\circ(\text{N}_2\text{O}_5)$$

$$\Delta H^\circ = (4 \text{ mol})(33.8 \text{ kJ/mol}) + (1 \text{ mol})(0.0 \text{ kJ/mol}) - (2 \text{ mol})(11 \text{ kJ/mol})$$

$$\Delta H^\circ = 113 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

238

**Ex. (cont.)**

**Step 2: Calculate**

$$\Delta n_{\text{gas}} = (n_{\text{gas}})_{\text{products}} - (n_{\text{gas}})_{\text{reactants}}$$

$$\Delta n_{\text{gas}} = (4 + 1 - 2) \text{ mol} = 3 \text{ mol}$$

**Step 3: Calculate  $\Delta E$  using**

$$R = 8.31451 \text{ J/K}\cdot\text{mol} \quad T = 298 \text{ K}$$

$$\Delta E = \Delta H - \Delta n_{\text{gas}}RT$$

$$\Delta E = 113 \text{ kJ} -$$

$$(3 \text{ mol})(8.31451 \text{ J/K}\cdot\text{mol})(298 \text{ K})(1 \text{ kJ}/1000 \text{ J})$$

$$\Delta E = 113 \text{ kJ} - 7.43 \text{ kJ} = 106 \text{ kJ}$$

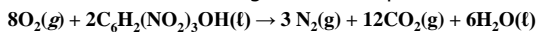
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

239

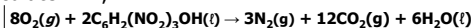
## Learning Check

**Ex.** Consider the following reaction for picric acid:



▪ What type of reaction is it?

▪ Calculate  $\Delta H^\circ$ ,  $\Delta E^\circ$



$\Delta H_f^\circ$ (kJ/mol)	0.00	3862.94	0.00	-393.5	-241.83
--------------------------------	------	---------	------	--------	---------

$$\Delta H^\circ = 12\text{mol}(-393.5 \text{ kJ/mol}) + 6\text{mol}(-241.83\text{kJ/mol}) + 6\text{mol}(0.00\text{kJ/mol}) - 8\text{mol}(0.00\text{kJ/mol}) - 2\text{mol}(3862.94\text{kJ/mol})$$

$$\Delta H^\circ = -13,898.9 \text{ kJ (Exothermic reaction)}$$

$$\Delta E^\circ = \Delta H^\circ - \Delta n_{\text{gas}}RT = \Delta H^\circ - (15 - 8)\text{mol}\cdot 298\text{ K} \cdot 8.314 \times 10^{-3}$$

$$\Delta E^\circ = -13,898.9 \text{ kJ} - 29.0 \text{ kJ} = -13,927.9 \text{ kJ}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

240



## Chapter 4

### Chemical Kinetics

Chemistry: The Molecular Nature  
of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

### Speeds at Which Reactions Occur

#### Kinetics:

- Study of factors that govern
  - How **rapidly** reactions occur **and**
  - How reactants **change** into products

#### Rate of Reaction:

- **Speed** with which reaction occurs
- How quickly reactants disappear and products form

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

242

---

---

---

---

---

---

---

### Factors that Affect Reaction Rates

#### 1. Chemical nature of reactants

- **What** elements, compounds, salts are **involved**?
- What **bonds** must be **formed, broken**?
- What are **fundamental differences** in chemical reactivity?

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

243

---

---

---

---

---

---

---

## Factors that Affect Reaction Rates

### 2. Ability of reactants to come in contact

- If two or more reactants **must meet** in order to react
- **Gas** or **solution** phase facilitates this
  - **Reactants** mix and collide with each other easily
- **Homogeneous reaction**
  - All reactants in **same** phase
  - Occurs rapidly
- **Heterogeneous reaction**
  - Reactants in **different** phases
  - Reactants meet only at **interface** between phases
  - Surface area determines reaction **rate**
  - $\uparrow$  area,  $\uparrow$  rate                       $\downarrow$  area,  $\downarrow$  rate

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

244

---

---

---

---

---

---

---

## Factors that Affect Reaction Rates

### 3. Concentrations of reactants

- Rates of both homogeneous and heterogeneous reactions affected by  $[X]$
- Collision rate between A and B  $\uparrow$  if we  $\uparrow [A]$  or  $\uparrow [B]$ .
  - $\therefore$  Often (but not always)
  - Reaction rate  $\uparrow$  as  $[X] \uparrow$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

245

---

---

---

---

---

---

---

## Factors that Affect Reaction Rates

### 4. Temperature

- Rates are often very sensitive to T
  - Cooking sugar
- Raising **T** usually makes reaction faster for two reasons:
  - a. Faster molecules collide more often and collisions have more **Energy**
  - b. Most reactions, even exothermic reactions, require **Energy** to get going

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

246

---

---

---

---

---

---

---

## Factors that Affect Reaction Rates

### 5. Presence of Catalysts

#### ▪ Catalysts

- Substances that ↑ rates of chemical and biochemical reactions without being used up
- Rate-accelerating agents
- Speed up rate dramatically

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

247

---

---

---

---

---

---

---

## Measuring Rate of Reaction

#### ▪ Rate of Chemical Reaction

- ↓ in [X] of particular species per unit time.

$$\text{reaction rate} = \frac{\Delta[\text{reactant}]}{\Delta \text{time}}$$

- Always **with respect to (WRT)** given reactant or product
- [reactants] ↓ w/ time
- [products] ↑ w/ time

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

248

---

---

---

---

---

---

---

## Rate of Reaction with Respect to Given Species X

$$\text{Rate WRT X} = \frac{[X]_{t_2} - [X]_{t_1}}{t_2 - t_1} = \frac{\Delta[X]}{\Delta t}$$

- Concentration in **M**

WRT: with respect to

- Time in **s**

$$\text{Units on rate: } \frac{\text{mol/L}}{\text{s}} = \frac{\text{mol}}{\text{L} \cdot \text{s}} = \frac{\text{M}}{\text{s}}$$

- **Ex.**

- [product] ↑ by 0.50 mol/L per **second** ⇒  
rate = 0.50 M/s

- [reactant] ↓ by 0.20 mol/L per **second** ⇒  
rate = 0.20 M/s

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

249

---

---

---

---

---

---

---

## Rate of Reaction

- **Always +**
  - Whether something is  $\uparrow$  or  $\downarrow$  in  $[X]$ .
- **Reactants**
  - Need  $-$  sign to make **rate +**
  - Reactant consumed
  - So  $\Delta[X] = -$ 

$$\text{Rate} = - \frac{\Delta[\text{reactant}]}{\Delta t}$$
- **Products**
  - Produced as reaction goes along
  - So  $\Delta[X] = +$
  - Thus Rate = **+**

$$\text{Rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

250

---

---

---

---

---

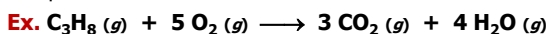
---

---

---

## Rates and Coefficients

- Relative rates at which reactants are consumed and products are formed
- Related by coefficients in balanced chemical equation.
- Know rate with respect to one product or reactant
- Can use equation to determine rates WRT all other products and reactants.



### Rate of Reaction

$$= - \frac{\Delta[\text{C}_3\text{H}_8]}{\Delta t} = - \frac{1}{5} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{4} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

251

---

---

---

---

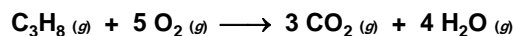
---

---

---

---

## Rates and Coefficients



- $\text{O}_2$  **reacts 5** times as fast as  $\text{C}_3\text{H}_8$ 

$$\text{Rate} = - \frac{\Delta[\text{O}_2]}{\Delta t} = -5 \frac{\Delta[\text{C}_3\text{H}_8]}{\Delta t}$$
- $\text{CO}_2$  **forms 3** times faster than  $\text{C}_3\text{H}_8$  **consumed**

$$\text{Rate} = \frac{\Delta[\text{CO}_2]}{\Delta t} = -3 \frac{\Delta[\text{C}_3\text{H}_8]}{\Delta t}$$
- $\text{H}_2\text{O}$  **forms 4/5** as fast as  $\text{O}_2$  **consumed**

$$\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = - \frac{4}{5} \frac{\Delta[\text{O}_2]}{\Delta t}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

252

---

---

---

---

---

---

---

---

## Rates and Coefficients

In general



$$\text{Rate} = -\frac{1}{\alpha} \frac{\Delta A}{\Delta t} = -\frac{1}{\beta} \frac{\Delta B}{\Delta t} = \frac{1}{\gamma} \frac{\Delta C}{\Delta t} = \frac{1}{\delta} \frac{\Delta D}{\Delta t}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

253

---

---

---

---

---

---

---

## Your Turn!

**Ex.** In the reaction  $2\text{CO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)}$ , the rate of the reaction of CO is measured to be 2.0 M/s. What would be the rate of the reaction of  $\text{O}_2$ ?

- A. the same = 2.0 M/s
- B. twice as great = 4.0 M/s
- C. half as large = 1.0 M/s
- D. you cannot tell from the given information

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

254

---

---

---

---

---

---

---

## Change of Reaction Rate with Time

- Generally reaction rate changes during reaction
  - i.e. Not constant
- Often initially fast when lots of reactant present
- Slower at end when reactant used up

### Why?

- Rate depends on [reactants]
- Reactants being used up, so [reactant] is ↓
- **[A]** vs. **time** is curve
- **A** is reactant ∴ [A] is ↓ w/ time

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

255

---

---

---

---

---

---

---

## Measuring Rates

- Measured in three ways:
  - Instantaneous rate
  - Average rate
  - Initial rate

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

256

---

---

---

---

---

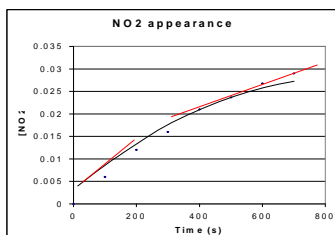
---

---

---

## Instantaneous Reaction Rates

- Instantaneous rate**
  - Slope of tangent to curve at any specific time
- Initial rate**
  - Determined at initial time



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

257

---

---

---

---

---

---

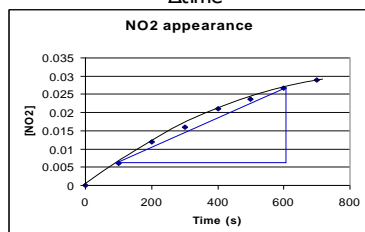
---

---

## Average Rate of Reaction

- Slope of line connecting starting and ending coordinates for specified time frame

$$\frac{\Delta[\text{Product}]}{\Delta\text{time}} = \text{rate}$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

258

---

---

---

---

---

---

---

---

**Table 14.1 Data at 508 °C**

**Ex. 2**  $\text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$

[HI] (mol/L)	Time (s)	Initial rate rate between first two data points
0.100	0	
0.0716	50	
0.0558	100	$\text{rate} = - \frac{(0.0716 - 0.100)\text{M}}{(50 - 0)\text{s}}$ $= \frac{-(-0.0284\text{M})}{50\text{s}}$ $= 5.68 \times 10^{-4} \text{M/s}$
0.0457	150	
0.0387	200	
0.0336	250	
0.0296	300	
0.0265	350	

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

259

---

---

---

---

---

---

---

---

**Rate at 300 s**

[HI] (mol/L)	Time (s)	$2 \text{HI}(g) \rightarrow \text{H}_2(g) + \text{I}_2(g)$ Rate = tangent of curve at 300 s
0.100	0	
0.0716	50	
0.0558	100	$\text{Rate} = - \frac{(0.0265 - 0.0296)\text{M}}{(350 - 300)\text{s}}$ $= \frac{0.0031\text{M}}{50\text{s}}$ $= 6.20 \times 10^{-5} \text{M/s}$
0.0457	150	
0.0387	200	
0.0336	250	
0.0296	300	
0.0265	350	

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

260

---

---

---

---

---

---

---

---

**Your Turn!**

**Ex.** The concentration of  $\text{NO}_2$  was found to be  $0.0258\text{M}$  at 5 minutes and at 10 minutes the concentration was  $0.0097\text{M}$ . What is the average rate of the reaction between 5 min and 10 min?

- A.  $310 \text{ M/min}$
- B.  $3.2 \times 10^{-3} \text{ M/min}$
- C.  $2.7 \times 10^{-3} \text{ M/min}$
- D.  $7.1 \times 10^{-3} \text{ M/min}$

$$\frac{(0.0258\text{M} - 0.0097\text{M})}{10\text{min} - 5\text{min}} = 3.2 \times 10^{-3} \text{M/min}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

261

---

---

---

---

---

---

---

---

## Concentration and Rate

### Rate Laws



- Homogeneous reaction
- Rate =  $k[A]^m[B]^n$** 
  - Rate Law or Rate expression
  - $m$  and  $n$  = exponents found experimentally
  - No necessary connection between stoichiometric coefficients ( $\alpha, \beta$ ) and rate exponents ( $m, n$ )
  - Usually small integers 1, 2, .....
  - Sometimes simple fractions ( $1/2, 3/4$ ) or zero

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

262

---

---

---

---

---

---

---

### Rate Laws

$$\text{Rate} = k[A]^m[B]^n$$

- Exponents tell **Order of Reaction** with respect to (**WRT**) each reactant
- Order of Reaction**
  - $m = 1$   $[A]^1$  1<sup>st</sup> order
  - $m = 2$   $[A]^2$  2<sup>nd</sup> order
  - $m = 3$   $[A]^3$  3<sup>rd</sup> order
  - $m = 0$   $[A]^0$  0<sup>th</sup> order
    - $[A]^0 = 1 \Rightarrow$  means **A doesn't affect rate**
- Overall order of reaction**
- sum of orders ( $m$  and  $n$ ) of each reactant in rate law

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

263

---

---

---

---

---

---

---

### Learning Check

**Ex.** The rate law for the reaction  $2A + B \rightarrow 3C$  is  
 $\text{rate} = k[A][B]$

If the concentration of A is 0.2M and that of B is 0.3M, and rate constant is  $0.045 \text{ M}^{-1}\text{s}^{-1}$  what will be the reaction rate?

$$\text{rate} = 0.045 \text{ M}^{-1} \text{ s}^{-1} [0.2][0.3]$$

$$\text{rate} = 0.0027 \text{ M/s} \Rightarrow 0.003 \text{ M/s}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

264

---

---

---

---

---

---

---



### Ex.



$$-\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{BrO}_3^-]^x[\text{Br}^-]^y[\text{H}^+]^z$$

- $x = 1$     $y = 1$     $z = 2$
- 1<sup>st</sup> order WRT  $\text{BrO}_3^-$
- 1<sup>st</sup> order WRT  $\text{Br}^-$
- 2<sup>nd</sup> order WRT  $\text{H}^+$
- Overall order =  $1 + 1 + 2 = 4$

$$\text{rate} = k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

265

---

---

---

---

---

---

---

---

### Ex.

- Sometimes  $n$  and  $m$  are coincidentally the same as stoichiometric coefficients



$$\text{rate} = -\frac{\Delta[\text{HI}]}{\Delta t} = k[\text{HI}]^2$$

- 2<sup>nd</sup> order WRT HI
- 2<sup>nd</sup> order overall

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

266

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** The following rate law has been observed:  
Rate =  $k[\text{H}_2\text{SeO}][\text{I}^-]^3[\text{H}^+]^2$ . The rate with respect to  $\text{I}^-$  and the overall reaction rate is:

- A. 6, 2
- B. 2, 3
- C. 1, 6
- D. 3, 6

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

267

---

---

---

---

---

---

---

---

## Calculating $k$ from Rate Law

- If we know rate and concentrations, can use rate law to calculate  $k$

**Ex.** at 508 °C

- Rate =  $2.5 \times 10^{-4} \text{ M/s}$
- $[\text{HI}] = 0.0558 \text{ M}$

$$\text{rate} = -\frac{\Delta[\text{HI}]}{\Delta t} = k[\text{HI}]^2$$

$$k = \frac{\text{rate}}{[\text{HI}]^2} = \frac{2.5 \times 10^{-4} \text{ M/s}}{(0.0558 \text{ M})^2} = 0.0802 \text{ M}^{-1} \text{ s}^{-1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

268

---

---

---

---

---

---

---

---

## How To Determine Exponents in Rate Law

### Experiments

- Method of Initial Rates
- If reaction is sufficiently slow
  - or have very fast technique
- Can measure  $[\text{A}]$  vs. time at very beginning of reaction
  - before it curves up very much, then

$$\text{initial rate} = -\left(\frac{[\text{A}]_1 - [\text{A}]_0}{t_1 - t_0}\right)$$

- Set up series of experiments, where initial concentrations vary

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

269

---

---

---

---

---

---

---

---

## Ex. Method of Initial Rates



**Rate =  $k[\text{A}]^m[\text{B}]^n$**

Expt. #	$[\text{A}]_0, \text{M}$	$[\text{B}]_0, \text{M}$	Initial Rate, $\text{M/s}$
1	0.10	0.10	$1.2 \times 10^{-4}$
2	0.20	0.10	$4.8 \times 10^{-4}$
3	0.20	0.20	$4.8 \times 10^{-4}$

- Convenient to set up experiments so
  - $[\text{X}]$  of one species is doubled or tripled
  - while  $[\text{X}]$  of all other species are held constant
- Tells us effect of [varied species] on initial rate

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

270

---

---

---

---

---

---

---

---

## Reaction Order and Rate

- If reaction is **1<sup>st</sup>** order WRT given species **X**,
  - Doubling  $[X]^1 \rightarrow 2^1$
  - Rate doubles
- If reaction is **2<sup>nd</sup>** order WRT **X**,
  - Doubling  $[X]^2 \rightarrow 2^2$
  - Rate quadruples
- If reaction is **0<sup>th</sup>** order WRT **X**,
  - Doubling  $[X]^0 \rightarrow 2^0$
  - Rate doesn't change
- If reaction is **n<sup>th</sup>** order WRT **X**
  - Doubling  $[X]^n \rightarrow 2^n$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

271

---

---

---

---

---

---

---

---

## Back to our Example

Expt. #	$[A]_0, M$	$[B]_0, M$	Initial Rate, $M/s$
1	0.10	0.10	$1.2 \times 10^{-4}$
2	0.20	0.10	$4.8 \times 10^{-4}$
3	0.20	0.20	$4.8 \times 10^{-4}$

### Comparing 1 and 2

- Doubling  $[A]$
- Quadruples rate
- Reaction **2<sup>nd</sup>** order in A
- $[A]^2$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.8 \times 10^{-4}}{1.2 \times 10^{-4}} = 4$$

$$4 = \frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[A_2]^m[B_2]^n}{k[A_1]^m[B_1]^n} = \frac{k[0.20]^m[0.10]^n}{k[0.10]^m[0.10]^n} = \frac{[0.20]^m}{[0.10]^m} = 2^m$$

$$2^m = 4 \quad \text{or} \quad m = 2$$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

272

---

---

---

---

---

---

---

---

## Back to our Example

Expt. #	$[A]_0, M$	$[B]_0, M$	Initial Rate, $M/s$
1	0.10	0.10	$1.2 \times 10^{-4}$
2	0.20	0.10	$4.8 \times 10^{-4}$
3	0.20	0.20	$4.8 \times 10^{-4}$

### Comparing 2 and 3

- Doubling  $[B]$
- Rate does not change
- Reaction **0<sup>th</sup>** order in B
- $[B]^0$

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{4.8 \times 10^{-4}}{4.8 \times 10^{-4}} = 1$$

$$1 = \frac{\text{Rate 3}}{\text{Rate 2}} = \frac{k[A_3]^m[B_3]^n}{k[A_2]^m[B_2]^n} = \frac{k[0.20]^m[0.20]^n}{k[0.20]^m[0.10]^n} = \frac{[0.20]^n}{[0.10]^n} = 2^n$$

$$2^n = 1 \quad \text{or} \quad n = 0$$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

273

---

---

---

---

---

---

---

---

### Ex. Method of Initial Rates

Expt. #	[A] <sub>0</sub> , M	[B] <sub>0</sub> , M	Initial Rate, M/s
1	0.10	0.10	$1.2 \times 10^{-4}$
2	0.20	0.10	$4.8 \times 10^{-4}$
3	0.20	0.20	$4.8 \times 10^{-4}$

- **Conclusion:** rate =  $k[A]^2$
- Can use data from any experiment to determine  $k$
- Let's choose experiment 1

$$k = \frac{\text{rate}}{[A]^2} = \frac{1.2 \times 10^{-4} \text{ M/s}}{(0.10 \text{ M})^2} = 1.2 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

274

---

---

---

---

---

---

---

---

### Ex. Method of Initial Rates



$$\text{Rate} = k[\text{SO}_2]^m[\text{O}_2]^n$$

Expt #	[SO <sub>2</sub> ], M	[O <sub>2</sub> ], M	Initial Rate of SO <sub>3</sub> formation, M·s <sup>-1</sup>
1	0.25	0.30	$2.5 \times 10^{-3}$
2	0.50	0.30	$1.0 \times 10^{-2}$
3	0.75	0.60	$4.5 \times 10^{-2}$
4	0.50	0.90	$3.0 \times 10^{-2}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

275

---

---

---

---

---

---

---

---

### Ex. Compare 1 and 2

- [SO<sub>2</sub>] doubles, [O<sub>2</sub>] constant,
- Rate quadruples, 2<sup>2</sup>

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.0 \times 10^{-2}}{2.5 \times 10^{-3}} = 4$$

$$4 = \frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[\text{SO}_2]_2^m[\text{O}_2]_2^n}{k[\text{SO}_2]_1^m[\text{O}_2]_1^n} = \frac{k[0.50]^m[0.30]^n}{k[0.25]^m[0.30]^n}$$

$$= \frac{[0.50]^m}{[0.25]^m} = 2^m \quad 2^m = 4 \quad \text{or} \quad m = 2$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

276

---

---

---

---

---

---

---

---

### Ex. Compare 2 and 4

- [O<sub>2</sub>] triples, [SO<sub>2</sub>] constant
- Rate triples, 3<sup>1</sup>

$$\frac{\text{Rate 4}}{\text{Rate 2}} = \frac{3.0 \times 10^{-2}}{1.0 \times 10^{-2}} = 3$$

$$3 = \frac{\text{Rate 4}}{\text{Rate 2}} = \frac{k[\text{SO}_2]_4^m [\text{O}_2]_4^n}{k[\text{SO}_2]_2^m [\text{O}_2]_2^n} = \frac{k[0.50]^m [0.90]^n}{k[0.50]^m [0.30]^n}$$

$$= \frac{[0.90]^n}{[0.30]^n} = 3^n \quad 3^n = 3 \quad \text{or} \quad n = 1$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

277

### Ex.

$$\text{Rate} = k[\text{SO}_2]^2[\text{O}_2]^1$$

- 1<sup>st</sup> order WRT O<sub>2</sub>
- 2<sup>nd</sup> order WRT SO<sub>2</sub>
- 3<sup>rd</sup> order overall
- Can use any experiment to find *k*

$$k = \frac{\text{rate}}{[\text{SO}_2]^2 [\text{O}_2]^1} = \frac{3.0 \times 10^{-2} \text{ M/s}}{(0.50 \text{ M})^2 (0.90 \text{ M})} = 0.13 \text{ M}^{-2} \text{ s}^{-1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

278

### Ex. Method of Initial Rates



$$\text{Rate} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{BrO}_3^-]^m [\text{Br}^-]^n [\text{H}^+]^p$$

Expt #	[BrO <sub>3</sub> <sup>-</sup> ], mol/L	[Br <sup>-</sup> ], mol/L	[H <sup>+</sup> ], mol/L	Initial Rate, mol/(L·s)
1	0.10	0.10	0.10	8.0 × 10 <sup>-4</sup>
2	0.20	0.10	0.10	1.6 × 10 <sup>-3</sup>
3	0.20	0.20	0.10	3.2 × 10 <sup>-3</sup>
4	0.10	0.10	0.20	3.2 × 10 <sup>-3</sup>

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

279

### Ex. Compare 1 and 2

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{1.6 \times 10^{-3} \text{ M/s}}{8.0 \times 10^{-4} \text{ M/s}} = \frac{k(0.20\text{M})^m (0.10\text{M})^n (0.10\text{M})^p}{k(0.10\text{M})^m (0.10\text{M})^n (0.10\text{M})^p}$$

$$2.0 = \left(\frac{0.20\text{M}}{0.10\text{M}}\right)^m = (2.0)^m \quad \therefore m = 1$$

### Compare 2 and 3

$$\frac{\text{Rate 3}}{\text{Rate 2}} = \frac{3.2 \times 10^{-3} \text{ M/s}}{1.6 \times 10^{-3} \text{ M/s}} = \frac{k(0.20\text{M})^m (0.20\text{M})^n (0.10\text{M})^p}{k(0.20\text{M})^m (0.10\text{M})^n (0.10\text{M})^p}$$

$$2.0 = \left(\frac{0.20\text{M}}{0.10\text{M}}\right)^n = (2.0)^n \quad \therefore n = 1$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

280

---

---

---

---

---

---

---

---

### Ex. Compare 1 and 4

$$\frac{\text{Rate 4}}{\text{Rate 1}} = \frac{3.2 \times 10^{-3} \text{ M/s}}{8.0 \times 10^{-4} \text{ M/s}} = \frac{k(0.10\text{M})^m (0.10\text{M})^n (0.20\text{M})^p}{k(0.10\text{M})^m (0.10\text{M})^n (0.10\text{M})^p}$$

$$4.0 = \left(\frac{0.20\text{M}}{0.10\text{M}}\right)^p = (2.0)^p \quad \therefore p = 2$$

- First order in  $[\text{BrO}_3^-]$  and  $[\text{Br}^-]$
- Second order in  $[\text{H}^+]$
- Overall order =  $m + n + p = 1 + 1 + 2 = 4$
- Rate Law is: **Rate =  $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

281

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** Using the following experimental data, determine the order with respect to  $\text{NO}$  and  $\text{O}_2$ .

Exp t #	$[\text{NO}]$ , M	$[\text{O}_2]$ , M	Initial Rate of $\text{NO}_2$ formation, $\text{M}\cdot\text{s}^{-1}$
1	0.12	0.25	$1.5 \times 10^{-3}$
2	0.24	0.25	$6.0 \times 10^{-3}$
3	0.50	0.50	$5.2 \times 10^{-2}$

- A. 2, 0
- B. 3, 1
- C. 2, 1
- D. 1, 1

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

282

---

---

---

---

---

---

---

---

## Your Turn! - Solution

$$\frac{R_2}{R_1} = \frac{6.0 \times 10^{-3} M s^{-1}}{1.5 \times 10^{-3} M s^{-1}} = \frac{[0.24M]^x [0.25M]^y}{[0.12M]^x [0.25M]^y}$$

$$x = 2$$

$$\frac{R_3}{R_1} = \frac{5.2 \times 10^{-2} M s^{-1}}{1.5 \times 10^{-3} M s^{-1}} = \frac{[0.50M]^2 [0.50M]^y}{[0.12M]^2 [0.25M]^y}$$

$$y = 1$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

283

## Concentration and Time

- Rate law tells us how speed of reaction varies with [X]'s.
- Sometimes want to know
  - [reactants] and [products] at given time during reaction
  - How long for [reactants] to drop below some minimum optimal value
- Need dependence of Rate on Time

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

284

## Concentration vs. Time for 1<sup>st</sup> Order Reactions

$$\text{Rate} = \frac{-\Delta[A]}{\Delta t} = k[A]$$

- Corresponding to reactions



- Integrating we get  $\ln \frac{[A]_0}{[A]_t} = kt$

- Rearranging gives  $\ln[A]_t = -kt + \ln[A]_0$

- Equation of line  $y = mx + b$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

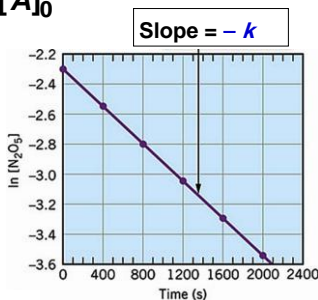
285

## Plot $\ln[A]_t$ (y axis) vs. $t$ (x axis)

$$\ln[A]_t = -kt + \ln[A]_0$$

- Yields straight line

- Indicative of 1<sup>st</sup> order kinetics
- slope =  $-k$
- intercept =  $\ln[A]_0$ 
  - If we don't know already



Jespersen/Brady/Hyslop

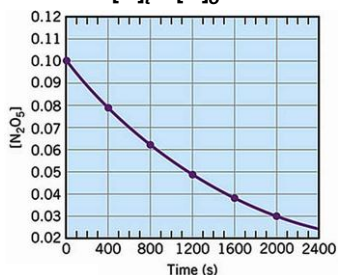
Chemistry: The Molecular Nature of Matter, 6E

285

## First Order Kinetics Graph

- Plot of  $[A]$  vs. time gives an exponential decay

$$[A]_t = [A]_0 e^{-kt}$$



JE

287

## Half-lives for 1<sup>st</sup> Order Reactions

- Half-life =  $t_{1/2}$

### First Order Reactions

- Set  $[A]_t = \frac{1}{2}[A]_0$

- Substituting into  $\ln \frac{[A]_0}{[A]_t} = kt$

- Gives  $\ln \frac{[A]_0}{\frac{1}{2}[A]_0} = kt_{1/2}$

- Canceling gives  $\ln 2 = kt_{1/2}$

- Rearranging gives  $t_{1/2} = \frac{\ln 2}{k_1} = \frac{0.693}{k_1}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

288



## Half-life for 1<sup>st</sup> Order Reactions

Observe:

1.  $t_{1/2}$  is **independent** of  $[A]_0$ 
  - For given reaction (and  $T$ )
  - Takes same time for concentration to fall from
    - 2  $M$  to 1  $M$  as from
    - $5.0 \times 10^{-3} M$  to  $2.5 \times 10^{-3} M$
2.  $k_1$  has units  $(\text{time})^{-1}$ , so  $t_{1/2}$  has units (time)
  - $t_{1/2}$  called **half-life**
  - Time for  $1/2$  of sample to decay

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

289

---

---

---

---

---

---

---

---

## Half-life for 1<sup>st</sup> Order Reactions

*Does this mean that all of sample is gone in two half-lives ( $2 \times t_{1/2}$ )?*

- No!
  - In **1<sup>st</sup>**  $t_{1/2}$ , it goes to  $1/2[A]_0$
  - In **2<sup>nd</sup>**  $t_{1/2}$ , it goes to  $1/2(1/2[A]_0) = 1/4[A]_0$
  - In **3<sup>rd</sup>**  $t_{1/2}$ , it goes to  $1/2(1/4[A]_0) = 1/8[A]_0$
  - In  **$n^{\text{th}}$**   $t_{1/2}$ , it goes to  $[A]_0/2^n$
- Existence of  $[X]$  independent **half-life** is property of exponential function
  - Property of 1<sup>st</sup> order kinetics

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

290

---

---

---

---

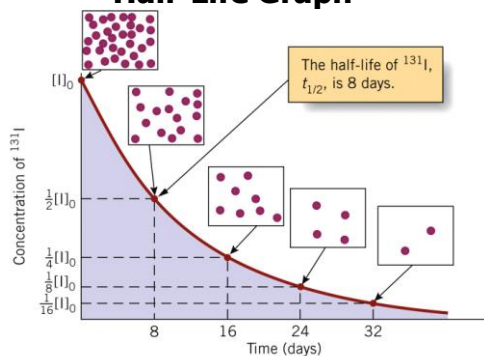
---

---

---

---

## Half-Life Graph



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

291

---

---

---

---

---

---

---

---

### Ex. Using Half-Life

- $^{131}\text{I}$  is used as a metabolic tracer in hospitals. It has a half-life,  $t_{1/2} = 8.07$  days. How long before the activity falls to 1% of the initial value?

$$N = N_0 e^{-kt}$$

$$\ln \frac{N}{N_0} = -kt = \frac{-t \ln 2}{t_{1/2}}$$

$$t = -\frac{t_{1/2} \ln \frac{N}{N_0}}{\ln 2} = -\frac{(8.07 \text{ days}) \ln \left( \frac{1}{100} \right)}{\ln 2} = 53.6 \text{ days}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

292

---

---

---

---

---

---

---

---

### Learning Check

**Ex.** The radioactive decay of a new atom occurs so that after 21 days, the original amount is reduced to 33%. What is the rate constant for the reaction in  $\text{s}^{-1}$ ?

$$\ln \left( \frac{A_0}{A} \right) = kt$$

$$\ln \left( \frac{100}{33} \right) = k(21 \text{ da})$$

$$k = 0.0528 \text{ da}^{-1}$$

$$k = 6.11 \times 10^{-7} \text{ s}^{-1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

293

---

---

---

---

---

---

---

---

### Learning Check

**Ex.** The half-life of I-132 is 2.295h. What percentage remains after 24 hours?

$$\frac{\ln(2)}{k} = t_{1/2} \quad k = \frac{\ln 2}{2.295 \text{ h}} \quad 0.302 \text{ h}^{-1} = k$$

$$\ln \left( \frac{A_0}{A} \right) = kt$$

$$\ln \left( \frac{A_0}{A} \right) = 0.302 \text{ h}^{-1} \times 24 \text{ h} = 7.248$$

$$A / A_0 = .0711 \%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

294

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Which order has a half-life that is independent of the original amount?

- A. Zero
- B. First
- C. Second
- D. None depend on the original quantity

---

---

---

---

---

---

---

## Theories about Reaction Rates

Reaction rate depends on [reactants] and T

### ▪ Collision Theory

- Based on Kinetic Molecular Theory
- Accounts for both effects on molecular level
- Central Idea
  - Molecules must collide to react
  - Greater number of collision/sec = greater reaction rate

---

---

---

---

---

---

---

## Theories about Reaction Rates

### ▪ Collision Theory

- As [reactants] ↑
  - number of Collisions ↑
  - Reaction rate ↑
- As T ↑
  - Molecular speed ↑
  - Molecules collide with more force (energy)
  - Reaction rate ↑

---

---

---

---

---

---

---

## Collision Theory

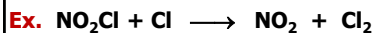
- Rate of reaction proportional to number of effective collisions/sec among reactant molecules

- Effective collision**

- that gives rise to product

### 1. Molecular Orientation

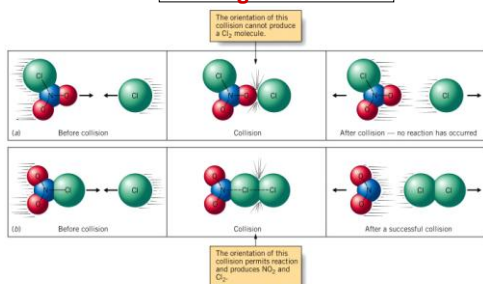
- Molecules must be oriented in a certain way during collisions for reaction to occur



- Cl must come in pointing directly at another Cl atom for  $\text{Cl}_2$  to form

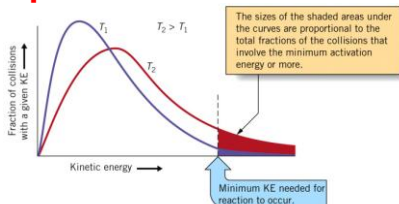
## Molecular Orientation

### Wrong Orientation



### Correct Orientation

## 2. Temperature



- Over moderate  $T$  range,  $E_a$  unchanged
- As  $\uparrow T$ ,
  - More molecules have  $E_a$
  - So more molecules undergo reaction
- Reaction rate  $\uparrow$  as  $T \uparrow$

### 3. Activation Energy, $E_a$

- Molecules must possess certain amount of kinetic energy (KE) in order to react

#### Activation Energy, $E_a$

- Minimum KE needed for reaction to occur

#### Transition State Theory

- Used to explain details of reactions
- What happens when reactant molecules collide

#### Potential Energy Diagram

- To visualize what actually happens during successful collision
- Relationship between  $E_a$  and developing Total PE

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

301

---

---

---

---

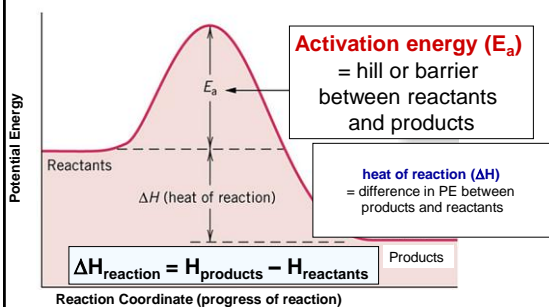
---

---

---

---

### Potential Energy Diagram



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

302

---

---

---

---

---

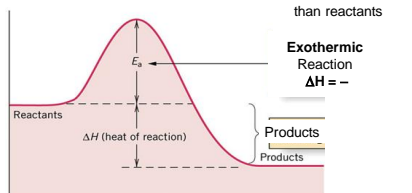
---

---

---

### Exothermic Reaction

- $\Delta H_{\text{reaction}} < 0$  (-)



- $E_a$  could be **high** and reaction **slow** even if  $\Delta H_{\text{rxn}}$  **large and negative**
- $E_a$  could be **low** and reaction **rapid**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

303

---

---

---

---

---

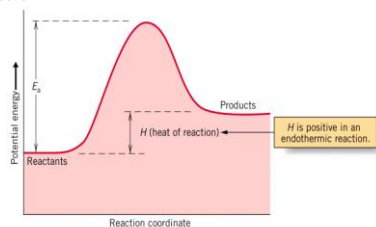
---

---

---

## Endothermic Reaction

$$\Delta H_{\text{reaction}} > 0 (+)$$



Endothermic  
Reaction  
 $\Delta H = +$

$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

304

---

---

---

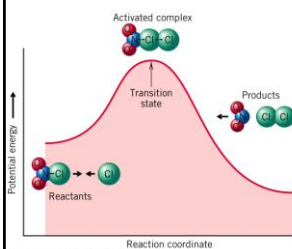
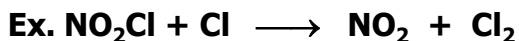
---

---

---

---

---



- As  $\text{NO}_2\text{Cl}$  and  $\text{Cl}$  come together
  - Start to form  $\text{Cl}\cdots\text{Cl}$  bond
  - Start to break  $\text{N}\cdots\text{Cl}$  bond
- Requires  $E_a$  as must bring 2 things together
- In TS
  - $\text{N}\cdots\text{Cl}$  bond  $\frac{1}{2}$  broken
  - $\text{Cl}\cdots\text{Cl}$  bond  $\frac{1}{2}$  formed
- After TS
  - $\text{Cl}-\text{Cl}$  bond forms
  - $\text{N}\cdots\text{Cl}$  breaks
- Releases  $E$  as products more stable

Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

305

---

---

---

---

---

---

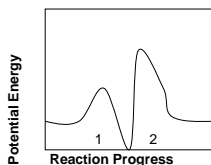
---

---

## Your Turn!

**Ex.** Examine the potential energy diagram. Which is the Slowest (Rate Determining) Step?

- A. Step 1
- B. Step 2 Has greatest  $E_a$
- C. Can't tell from the given information



Jespersen/Brady/Hyslop Chemistry: The Molecular Nature of Matter, 6E

306

---

---

---

---

---

---

---

---

## Measuring Activation Energy

### ▪ Arrhenius Equation

- Equation expressing **T** dependence of **k**

$$k = Ae^{-E_a/RT}$$

- **A** = Frequency factor—has same units as **k**
- **R** = gas constant in energy units  
 $= 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- **E<sub>a</sub>** = Activation Energy—has units of **J/mol**
- **T** = Temperature in **K**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

307

---

---

---

---

---

---

---

## How To Calculate Activation Energy

### ▪ Method 1. Graphically

- Take natural logarithm of both sides

- Rearranging

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) * \left(\frac{1}{T}\right)$$

- Equation for a line

$$y = b + m x$$

### **Arrhenius Plot**

- Plot **ln k** (**y** axis) vs. **1/T** (**x** axis)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

308

---

---

---

---

---

---

---

## Method 2. van't Hoff Equation

### ▪ van't Hoff Eq

### ▪ Equation

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

309

---

---

---

---

---

---

---

## Using van't Hoff Equation



$k$ (L/mol·s)	$T$ (°C)	$T$ (K)
$1.1 = k_1$	550	$823 = T_1$
$6.4 = k_2$	625	$898 = T_2$

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{-E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left( \frac{1}{898 \text{ K}} - \frac{1}{823 \text{ K}} \right)$$

$$E_a = \frac{-(8.314 \text{ J/K} \cdot \text{mol}) \ln\left(\frac{6.4}{1.1}\right)}{\left( \frac{1}{898 \text{ K}} - \frac{1}{823 \text{ K}} \right)} = 1.4 \times 10^5 \text{ J/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

310

---

---

---

---

---

---

---

---

## Learning Check

**Ex.** Given that  $k$  at 25°C is  $4.61 \times 10^{-1} \text{ M/s}$  and that at 50°C it is  $4.64 \times 10^{-1} \text{ M/s}$ , what is the activation energy for the reaction?

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln\left(\frac{4.64 \times 10^{-1} \text{ M/s}}{4.61 \times 10^{-1} \text{ M/s}}\right) = \frac{-E_a}{8.314 \text{ J/(mol} \cdot \text{K)}} \left( \frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$E_a = 208 \text{ J/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

311

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** A reaction has an activation energy of 40 kJ/mol. What happens to the rate if you increase the temperature from 70 °C to 80 °C?

- A. Rate increases approximately 1.5 times
- B. Rate increases approximately 5000 times
- C. Rate does not increase
- D. Rate increases approximately 3 times

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

312

---

---

---

---

---

---

---

---



## Your Turn! - Solution

Rate is proportional to the rate constant

$$\frac{k_2}{k_1} = \frac{e^{-\left(\frac{40000 \text{ J}}{8.314 \frac{\text{J}}{\text{mol K}} \times (80+273)\text{K}}\right)}}{e^{-\left(\frac{40000 \text{ J}}{8.314 \frac{\text{J}}{\text{mol K}} \times (70+273)\text{K}}\right)}} = 1.49$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

313

---

---

---

---

---

---

---

---

## Homogeneous Catalyst

- Same phase as reactants

Consider :  $\text{S (g)} + \text{O}_2 \text{ (g)} + \text{H}_2\text{O (g)} \longrightarrow \text{H}_2\text{SO}_4 \text{ (g)}$

$\text{S (g)} + \text{O}_2 \text{ (g)} \longrightarrow \text{SO}_2 \text{ (g)}$

$\text{NO}_2 \text{ (g)} + \text{SO}_2 \text{ (g)} \longrightarrow \text{NO (g)} + \text{SO}_3 \text{ (g)}$  Catalytic pathway

$\text{SO}_3 \text{ (g)} + \text{H}_2\text{O (g)} \longrightarrow \text{H}_2\text{SO}_4 \text{ (g)}$

$\text{NO (g)} + \frac{1}{2}\text{O}_2 \text{ (g)} \longrightarrow \text{NO}_2 \text{ (g)}$  Regeneration of catalyst

**Net:**  $\text{S (g)} + \text{O}_2 \text{ (g)} + \text{H}_2\text{O (g)} \longrightarrow \text{H}_2\text{SO}_4 \text{ (g)}$

- What is Catalyst?**  $\text{NO}_2 \text{ (g)}$

- Reactant** (used up) in early step
- Product** (regenerated) in later step

- Which are Intermediates?**  $\text{NO}$  and  $\text{SO}_3$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

314

---

---

---

---

---

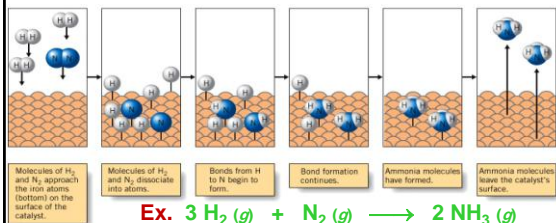
---

---

---

## Heterogeneous Catalyst

Exists in separate phase from reactants



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

**H<sub>2</sub> & N<sub>2</sub> approach Fe catalyst**

**H<sub>2</sub> & N<sub>2</sub> bind to Fe & bonds break**

**N—H bonds forming**

**N—H bonds forming**

**NH<sub>3</sub> formation complete**

**NH<sub>3</sub> dissociates**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

315

---

---

---

---

---

---

---

---

## Chapter 5

### Properties of Solutions

Chemistry: The Molecular Nature  
of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

## Solutions

### Solution

- Homogeneous mixture
- Composed of solvent and solute(s)

### Solvent

- More abundant component of mixture

### Solute(s)

- Less abundant or other component(s) of mixture

Ex. Lactated Ringer's solution

- NaCl, KCl, CaCl<sub>2</sub>, NaC<sub>3</sub>H<sub>5</sub>O<sub>3</sub> in water

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

317

---

---

---

---

---

---

---

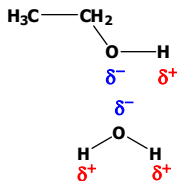
## Rule of Thumb

### ▪ "Like dissolves Like"

- Use **polar** solvent for **polar** solute
- Use **Nonpolar** solvent for **nonpolar** solute
- **Polar** solutes interact with and dissolve in **polar** solvents

Ex. Ethanol in water

- Both are polar molecules
- Both form hydrogen bonds



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

318

---

---

---

---

---

---

---

**miscible Solution Benzene in  $\text{CCl}_4$**

- $\text{CCl}_4$ 
  - Nonpolar
- Benzene,  $\text{C}_6\text{H}_6$ 
  - Nonpolar
    - Similar in strength to  $\text{CCl}_4$
- Does dissolve, solution forms

**Immiscible Solution Benzene in water**

- Solvent and solute are very "different"
- No solution forms
  - 2 layers, Don't Mix

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

319

---

---

---

---

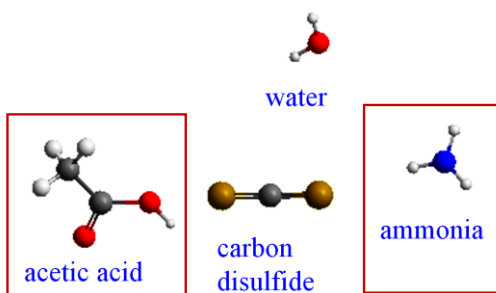
---

---

---

**Learning Check**

**Ex.** Which of the following are miscible in water?



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

320

---

---

---

---

---

---

---

**Your Turn!**

**Ex.** Which of the following molecules is soluble in  $\text{C}_6\text{H}_6$ ?

- A.  $\text{NH}_3$
- B.  $\text{CH}_3\text{NH}_2$
- C.  $\text{CH}_3\text{OH}$
- D.  $\text{CH}_3\text{CH}_3$
- E.  $\text{CH}_3\text{Cl}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

321

---

---

---

---

---

---

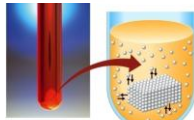
---

## Solubility

- Mass of solute that forms **saturated solution** with given mass of solvent at specified temperature

$$\text{solubility} = \frac{g \text{ solute}}{100g \text{ solvent}}$$

- If extra solute added to saturated solution, extra solute will remain as separate phase
- $\text{solute}_{\text{undissolved}} \rightleftharpoons \text{solute}_{\text{dissolved}}$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

322

---

---

---

---

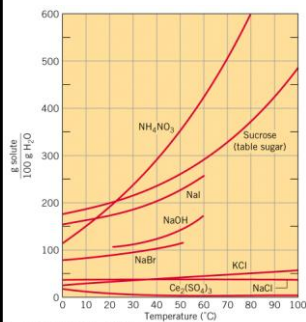
---

---

---

---

## Effect of T on solid Solubility in Liquids



- Most substances become more soluble as  $T \uparrow$
- Amount solubility  $\uparrow$ 
  - Varies considerably
  - Depends on substance

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Chemistry: The Molecular Nature of Matter, 6E

323

---

---

---

---

---

---

---

---

## Effect of T on Gas Solubility in Liquids

- Solubility of gases usually  $\downarrow$  as  $T \uparrow$**

**Table 13.2** Solubilities of Common Gases in Water

Gas	Temperature			
	0 °C	20 °C	50 °C	100 °C
Nitrogen, N <sub>2</sub>	0.0029	0.0019	0.0012	0
Oxygen, O <sub>2</sub>	0.0069	0.0043	0.0027	0
Carbon dioxide, CO <sub>2</sub>	0.335	0.169	0.076	0
Sulfur dioxide, SO <sub>2</sub>	22.8	10.6	4.3	1.8 <sup>b</sup>
Ammonia, NH <sub>3</sub>	89.9	51.8	28.4	7.4 <sup>c</sup>

<sup>a</sup>Solubilities are in grams of solute per 100 g of water when the gaseous space over the liquid is saturated with the gas and the total pressure is 1 atm.

<sup>b</sup>Solubility at 90 °C.

<sup>c</sup>Solubility at 96 °C.

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

324

---

---

---

---

---

---

---

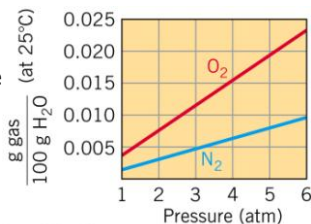
---

## Effect of **Pressure** on Gas Solubility

- **Solubility  $\uparrow$  as  $P \uparrow$**

**Why?**

- $\uparrow P$  means  $\downarrow V$  above solution for gas
- Gas goes into solution
  - Relieves stress on system
- Conversely, solubility  $\downarrow$  as  $P \downarrow$ 
  - Soda in can



Gases are more soluble at low temperature and high pressure.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

325

---

---

---

---

---

---

---

---

## Effect of **Pressure** on Gas Solubility

- A.** At some  $P$ , equilibrium exists between vapor phase and solution

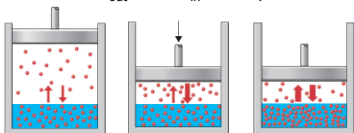
- $\text{rate}_{\text{in}} = \text{rate}_{\text{out}}$

- B.**  $\uparrow$  in  $P$  puts stress on equilibrium

- $\uparrow$  frequency of collisions so  $\text{rate}_{\text{in}} > \text{rate}_{\text{out}}$
- More gas molecules dissolve than are leaving solution

- C.** More gas dissolved

- $\text{Rate}_{\text{out}}$  will  $\uparrow$  until  $\text{Rate}_{\text{out}} = \text{Rate}_{\text{in}}$  and equilibrium restored



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

326

---

---

---

---

---

---

---

---

## Henry's Law

- Pressure-Solubility Law
- "Concentration of gas in liquid at any given temperature is directly proportional to partial pressure of gas over solution"

$$C_{\text{gas}} = k_H P_{\text{gas}} \quad (T \text{ is constant})$$

$C_{\text{gas}}$  = concentration of gas

$P_{\text{gas}}$  = partial pressure of gas

$k_H$  = Henry's Law constant

- Unique to each gas
- Tabulated

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

327

---

---

---

---

---

---

---

---

## Henry's Law

- True only at low concentrations and pressures where gases do NOT react with solvent

- Alternate form

$$\frac{C_1}{P_1} = \frac{C_2}{P_2}$$

- $C_1$  and  $P_1$  refer to an initial set of conditions
- $C_2$  and  $P_2$  refer to a final set of conditions

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

328

---

---

---

---

---

---

---

---

## Ex. Using Henry's Law

Calculate the concentration of  $\text{CO}_2$  in a soft drink that is bottled with a partial pressure of  $\text{CO}_2$  of 5 atm over the liquid at 25 °C. The Henry's Law constant for  $\text{CO}_2$  in water at this temperature is  $3.12 \times 10^{-2} \text{ mol/L} \cdot \text{atm}$ .

$$\begin{aligned} C_{\text{CO}_2} &= k_{\text{H}}(\text{CO}_2)P_{\text{CO}_2} \\ &= 3.12 \times 10^{-2} \text{ mol/L} \cdot \text{atm} * 5.0 \text{ atm} \\ &= 0.156 \text{ mol/L} \Rightarrow \mathbf{0.16 \text{ mol/L}} \end{aligned}$$

**When under 5.0 atm pressure**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

329

---

---

---

---

---

---

---

---

## Ex. Using Henry's Law

Calculate the concentration of  $\text{CO}_2$  in a soft drink after the bottle is opened and equilibrates at 25 °C under a partial pressure of  $\text{CO}_2$  of  $4.0 \times 10^{-4} \text{ atm}$ .

$$\begin{aligned} \frac{C_1}{P_1} &= \frac{C_2}{P_2} & C_2 &= \frac{P_2 C_1}{P_1} \\ C_2 &= \frac{(0.156 \text{ mol/L})(4.0 \times 10^{-4} \text{ atm})}{5.0 \text{ atm}} \end{aligned}$$

$$C_2 = \mathbf{1.2 \times 10^{-4} \cdot \text{mol/L}}$$

**When open to air**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

330

---

---

---

---

---

---

---

---

## Learning Check

**Ex.** What is the concentration of dissolved nitrogen in a solution that is saturated in  $N_2$  at 2.0 atm?  $k_H = 8.42 \times 10^{-7} \text{ (M / atm)}$

- $C_g = k_H P_g$
- $C_g = 8.42 \times 10^{-7} \text{ (M / atm)} \times 2.0 \text{ atm}$
- $C_g = 1.7 \times 10^{-6} \text{ M}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

331

---

---

---

---

---

---

---

## Your Turn!

**Ex.** How many grams of oxygen gas at 1.0 atm will dissolve in 10.0 L of water at 25 °C if Henry's constant is  $1.3 \times 10^{-3} \text{ M atm}^{-1}$  at this temperature?

- A. 0.42 g
- B. 0.013 g
- C. 0.042 g
- D. 0.21 g
- E. 2.4 g

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

332

---

---

---

---

---

---

---

## Colligative Properties

- Physical properties of solutions
- Depend mostly on relative populations of **particles** in mixtures
- Don't depend on their chemical identities

### Effects of Solute on Vapor Pressure of Solvents

- Solutes that can't evaporate from solution are called **nonvolatile solutes**

**Fact:** All solutions of **nonvolatile solutes** have lower vapor pressures than their pure solvents

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

333

---

---

---

---

---

---

---

## Raoult's Law

- Vapor pressure of solution,  $P_{\text{soln}}$  equals product of mole fraction of solvent,  $X_{\text{solvent}}$  and its vapor pressure when pure,  $P_{\text{solvent}}^{\circ}$
- Applies for dilute solutions

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

$P_{\text{solution}}$  = vapor pressure of the solution

$X_{\text{solvent}}$  = mole fraction of the solvent

$P_{\text{solvent}}^{\circ}$  = vapor pressure of pure solvent

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

334

---

---

---

---

---

---

---

---

## Alternate form of Raoult's Law

- Plot of  $P_{\text{soln}}$  vs.  $X_{\text{solvent}}$  should be **linear**

- Slope** =  $P_{\text{solvent}}^{\circ}$

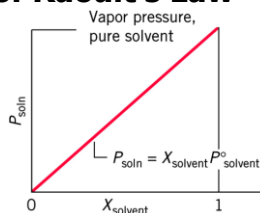
- Intercept** = 0

- Change in vapor pressure can be expressed as

$$\Delta P = \text{change in } P = (P_{\text{solvent}}^{\circ} - P_{\text{solution}})$$

- Usually more interested in how solute's mole fraction changes the vapor pressure of solvent

$$\Delta P = X_{\text{solute}} P_{\text{solvent}}^{\circ}$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

335

---

---

---

---

---

---

---

---

## Learning Check

**Ex.** The vapor pressure of 2-methylhexane is 37.986 torr at 15°C. What would be the pressure of the mixture of 78.0 g 2-methylhexane and 15 g naphthalene, which is nearly non-volatile at this temperature?



$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

$$\text{mole naphthalene} = \frac{15 \text{ g}}{128.17 \text{ g/mol}} = 0.117 \text{ mol}$$

$$\text{mole 2-methylhexane} = \frac{78.0 \text{ g}}{100.2 \text{ g/mol}} = 0.7784 \text{ mol}$$

$$X_{\text{2-methylhexane}} = \frac{0.7784 \text{ mol}}{0.7784 \text{ mol} + 0.117 \text{ mol}} = 0.869$$

$$P = (0.869 \times 37.986 \text{ torr})$$

$$= 33.02 \text{ torr} = \mathbf{33 \text{ torr}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

336

---

---

---

---

---

---

---

---



## Solutions That Contain Two or More Volatile Components

- Now vapor contains molecules of both components
  - Partial pressure of each component A and B is given by Raoult's Law

$$P_A = X_A P_A^\circ$$

$$P_B = X_B P_B^\circ$$

- Total pressure of solution of components A and B given by Dalton's Law of Partial Pressures

$$P_{total} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

337

---

---

---

---

---

---

---

---

## Ex. Benzene and Toluene

- Consider a mixture of benzene,  $C_6H_6$ , and toluene,  $C_7H_8$ , containing 1.0 mol benzene and 2.0 mol toluene. At 20 °C, the vapor pressures of the pure substances are:
  - $P_{benzene}^\circ = 75 \text{ torr}$
  - $P_{toluene}^\circ = 22 \text{ torr}$
- what is the total pressure above this solution?

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

338

---

---

---

---

---

---

---

---

## Ex. Benzene and Toluene (cont.)

### 1. Calculate mole fractions of A and B

$$X_{benzene} = \frac{1.0 \text{ mol}}{(1.0 + 2.0) \text{ mol}} = 0.33 \text{ benzene}$$

$$X_{toluene} = \frac{2.0 \text{ mol}}{(1.0 + 2.0) \text{ mol}} = 0.67 \text{ toluene}$$

### 2. Calculate partial pressures of A and B

$$P_{benzene} = X_{benzene} * P_{benzene}^\circ = 0.33 \times 75 \text{ torr} = 25 \text{ torr}$$

$$P_{toluene} = X_{toluene} * P_{toluene}^\circ = 0.67 \times 22 \text{ torr} = 15 \text{ torr}$$

### 3. Calculate total pressure

$$P_{total} = P_{benzene} + P_{toluene} \\ = (25 + 15) \text{ torr} = 40 \text{ torr}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

339

---

---

---

---

---

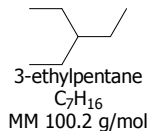
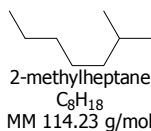
---

---

---

## Learning Check

**Ex.** The vapor pressure of 2-methylheptane is 233.95 torr at 55°C. 3-ethylpentane has a vapor pressure of 207.68 at the same temperature. What would be the pressure of the mixture of 78.0g 2-methylheptane and 15 g 3-ethylpentane?



$$P_{\text{solution}} = X_A P_A^\circ + X_B P_B^\circ$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

340

---

---

---

---

---

---

---

---

## Learning Check

$$\text{mole 2-methylheptane} = \frac{78.0 \text{ g}}{114.23 \text{ g/mol}} = 0.6828 \text{ mol}$$

$$\text{mole 3-ethylpentane} = \frac{15 \text{ g}}{100.2 \text{ g/mol}} = 0.1497 \text{ mol}$$

$$X_{2\text{-methylpentane}} = \frac{0.6828 \text{ mol}}{(0.6828 \text{ mol} + 0.1497 \text{ mol})} = 0.827$$

$$X_{3\text{-ethylpentane}} = \frac{0.1497 \text{ mol}}{(0.6828 \text{ mol} + 0.1497 \text{ mol})} = 0.173$$

$$P = (0.827 \times 233.95 \text{ torr}) + (0.173 \times 207.68 \text{ torr})$$

$$P = 230 \text{ torr}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

341

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** If the vapor pressure of pure hexane is 151.28 mmHg, and heptane is 45.67 mm Hg at 25°, which equation is correct if the mixture's vapor pressure is 145.5 mmHg?

- A.  $X(151.28 \text{ mmHg}) = 145.5 \text{ mmHg}$
- B.  $X(151.28 \text{ mmHg}) + (X)(45.67 \text{ mmHg}) = 145.5 \text{ mmHg}$
- C.  $X(151.28 \text{ mmHg}) + (1 - X)(45.67 \text{ mmHg}) = 145.5 \text{ mmHg}$
- D. None of these

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

342

---

---

---

---

---

---

---

---

## Solutes also Affect Freezing and Boiling Points of Solutions

- **Freezing Point** of solution always **Lower** than pure solvent
- **Boiling Point** of solution always **Higher** than pure solvent

### Colligative properties

- **Boiling Point Elevation ( $\Delta T_b$ )**
  - $\uparrow$  in boiling point of solution vs. pure solvent
- **Freezing Point Depression ( $\Delta T_f$ )**
  - $\downarrow$  in freezing point of solution vs. pure solvent

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

343

---

---

---

---

---

---

---

---

## Freezing Point Depression ( $\Delta T_f$ )

$$\Delta T_f = K_f m$$

where

$$\Delta T_f = (T_{fp} - T_{soln})$$

$m$  = concentration in Molality

$K_f$  = molal freezing point depression constant

Units of  $^{\circ}\text{C/molal}$ , Depend on solvent.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

344

---

---

---

---

---

---

---

---

## Boiling Point Elevation ( $\Delta T_b$ )

$$\Delta T_b = K_b m$$

where

$$\Delta T_b = (T_{soln} - T_{bp})$$

$m$  = concentration in Molality

$K_b$  = molal boiling point elevation constant

Units of  $^{\circ}\text{C}/m$ , Depend on solvent.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

345

---

---

---

---

---

---

---

---

## Values of $K_f$ and $K_b$ for solvents

Table 13.3 Molal Boiling Point Elevation and Freezing Point Depression Constants

Solvent	BP (°C)	$K_b$ (°C $m^{-1}$ )	MP (°C)	$K_f$ (°C $m^{-1}$ )
Water	100	0.51	0	1.86
Acetic acid	118.3	3.07	16.6	3.90
Benzene	80.2	2.53	5.45	5.07
Chloroform	61.2	3.63	-63.5	4.68
Camphor	—	—	178.4	39.7
Cyclohexane	80.7	2.69	6.5	20.2

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

346

### Ex. Freezing Point Depression

Estimate the freezing point of solution contain 100.0 g ethylene glycol,  $C_2H_6O_2$ , (MM = 62.07) and 100.0 g  $H_2O$  (MM = 18.02).

$$100.0g C_2H_6O_2 \times \frac{1mol C_2H_6O_2}{62.07g C_2H_6O_2} = 1.611mol C_2H_6O_2$$

$$m = \frac{mol \text{ solute}}{kg \text{ solvent}} = \frac{1.611mol C_2H_6O_2}{0.100kg \text{ water}} = 16.11m C_2H_6O_2$$

$$\Delta T_f = K_f m = (1.86 ^\circ C/m) \times 16.11m = 30.0 ^\circ C$$

$$\Delta T_f = (T_{fp} - T_{soln})$$

$$30.0 ^\circ C = 0.0 ^\circ C - T_{soln}$$

$$T_{soln} = 0.0 ^\circ C - 30.0 ^\circ C = \mathbf{-30.0 ^\circ C}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

347

### Your Turn!

- Ex. When 0.25 g of an unknown organic compound is added to 25.0 g of cyclohexane, the freezing point of cyclohexane is lowered by 1.6 °C.  $K_f$  for the solvent is 20.2 °C  $m^{-1}$ . Determine the molar mass of the unknown.

A. 505 g/mol  $\Delta T_f = K_f m$

B. 32 g/mol

C. 315 g/mol

D. 126 g/mol

$$1.6 ^\circ C = 20.2 \frac{^\circ C}{m} \times \frac{\left[ \frac{0.250 g}{MW} \right]}{0.025 kg}$$

$$MW = 126 g/mol$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

348

## Ex. Boiling Point Elevation

A 2.00 g biomolecule sample was dissolved in 15.0 g of  $\text{CCl}_4$ . The boiling point of this solution was determined to be 77.85 °C. Calculate the molar mass of the biomolecule. For  $\text{CCl}_4$ , the  $K_b = 5.07\text{ }^\circ\text{C}/m$  and  $\text{BP}_{\text{CCl}_4} = 76.50\text{ }^\circ\text{C}$ .

$$\Delta T_b = K_b m \quad m = \frac{\Delta T_b}{K_b} = \frac{(77.85 - 76.50)^\circ\text{C}}{5.07^\circ\text{C} / m} = 0.2684m$$
$$m = \frac{\text{mol solute}}{\text{kg solvent}} \quad \text{mol solute} = 0.2684m \times 0.0150\text{kg CCl}_4$$
$$= 4.026 \times 10^{-3} \text{ mol}$$

$$\text{MM}_{\text{biomolecule}} = \frac{2.00\text{g biomolecule}}{4.026 \times 10^{-3} \text{ mole}} = 497\text{g / mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

349

---

---

---

---

---

---

---

---

## Osmosis

### Osmotic Membrane

- Semipermeable membrane that lets only solvent molecules through

### Osmosis

- Net shift of solvent molecules (usually water) through an osmotic membrane
- Direction of flow in osmosis,
  - Solvent flows *from dilute to more* concentrated side
  - Flow of solvent molecules across osmotic membrane
    - ↑ concentration of solute on *dilute* side
    - ↓ concentration of solute on *more concentrated* side

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

350

---

---

---

---

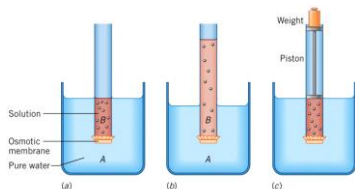
---

---

---

---

## Osmosis and Osmotic Pressure



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

- A.** Initially, Soln B separated from pure water, A, by osmotic membrane. No osmosis occurred yet
- B.** After a while, volume of fluid in tube higher. Osmosis has occurred.
- C.** Need back pressure to prevent osmosis = **osmotic pressure**.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

351

---

---

---

---

---

---

---

---

## Equation for Osmotic Pressure

- Assumes dilute solutions

$$\Pi = MRT$$

- $\Pi$  = osmotic pressure
- $M$  = molarity of solution
- $T$  = Kelvin Temperature
- $R$  = Ideal Gas constant  
=  $0.082057 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

352

---

---

---

---

---

---

---

---

## Ex. Using $\Pi$ to determine MM

A solution contained 3.50 mg of protein in sufficient  $\text{H}_2\text{O}$  to form 5.00 mL of solution. The measured osmotic pressure of this solution was 1.54 torr at 25 °C. Calculate the molar mass of the protein.

$$M = \frac{\Pi}{RT} = \frac{1.54 \text{ torr} \left( \frac{1 \text{ atm}}{760 \text{ torr}} \right)}{\left( 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) 298 \text{ K}} = 8.28 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$\text{mol} = M \cdot L = (8.28 \times 10^{-5} \text{ M}) \cdot 5.00 \times 10^{-3} \text{ L} = 4.14 \times 10^{-7} \text{ mol}$$

$$\text{MM} = \frac{g}{\text{mol}} = \frac{3.50 \times 10^{-3} \text{ g}}{4.14 \times 10^{-7} \text{ mol}} = 8.45 \times 10^3 \text{ g/mol}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

353

---

---

---

---

---

---

---

---

## Learning Check

Ex. For a typical blood plasma, the osmotic pressure at body temperature (37°C) is 5409 mm Hg. If the dominant solute is serum protein, what is the concentration of serum protein?

$$\Pi = MRT$$

$$\frac{5409 \text{ mm Hg}}{760 \text{ mm Hg}} \times \frac{1 \text{ atm}}{1 \text{ atm}} = \Pi$$

$$7.117 \text{ atm} = \frac{? \text{ mol}}{\text{L}} \times \frac{0.082057 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 310.15 \text{ K}$$

$$M = 0.280 \text{ M}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

354

---

---

---

---

---

---

---

---

## Chapter 6

### Chemical Equilibrium

Chemistry: The Molecular Nature  
of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

### Dynamic Equilibrium in Chemical Systems

- Chemical equilibrium exists when
  - Rates of forward and reverse reactions are equal
  - Reaction appears to stop
  - [reactants] and [products] don't change over time
    - Remain constant
    - Both forward and reverse reaction never cease
- Equilibrium signified by double arrows ( $\rightleftharpoons$ ) or equal sign (=)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

356

---

---

---

---

---

---

---

### Dynamic Equilibrium



- Initially forward reaction rapid
  - As some reacts  $\downarrow$  [N<sub>2</sub>O<sub>4</sub>] so rate forward  $\downarrow$
- Initially Reverse reaction slow
  - No products
- As NO<sub>2</sub> forms
  - $\uparrow$  Reverse rate
  - Ions collide more frequently as [ions]  $\uparrow$
- Eventually **rate**<sub>forward</sub> = **rate**<sub>reverse</sub>
  - Equilibrium

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

357

---

---

---

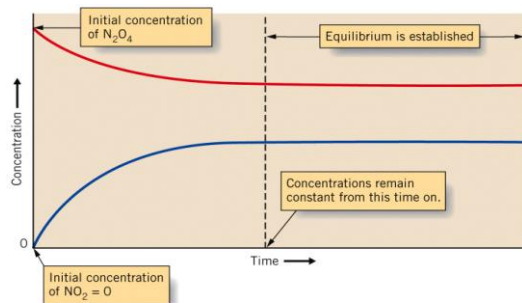
---

---

---

---

## Dynamic Equilibrium



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

358

---

---

---

---

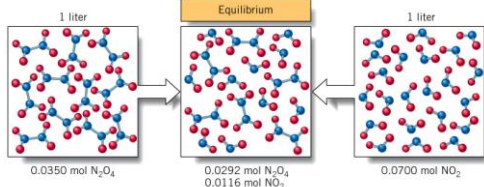
---

---

---

---

## Reactants      Equilibrium      Products



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.



- For given overall system composition
- Always reach same equilibrium concentrations
- Whether equilibrium is approached from **forward** or **reverse** direction

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

359

---

---

---

---

---

---

---

---

## Equilibrium

- Simple relationship among [**reactants**] and [**products**] for any chemical system at equilibrium
- Called = **mass action expression**
  - Derived from thermodynamics
- Forward reaction:  $\text{A} \rightarrow \text{B}$       **Rate** =  $k_f[\text{A}]$
- Reverse reaction:  $\text{A} \xleftarrow{k_r} \text{B}$       **Rate** =  $k_r[\text{B}]$
- At equilibrium:  $\text{A} \rightleftharpoons \text{B}$        $k_f[\text{A}] = k_r[\text{B}]$ 
  - rate forward** = **rate reverse**
- rearranging:

$$\frac{[\text{B}]}{[\text{A}]} = \frac{k_f}{k_r} = \underline{\text{constant}}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

360

---

---

---

---

---

---

---

---



## Mass Action Expression (MAE)

- Uses stoichiometric coefficients as exponent for each reactant
- For reaction:  $aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

### Reaction quotient

- Numerical value of mass action expression
- Equals "Q" at any time, **and**
- Equals "K" only when reaction is known to be at equilibrium

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

361

---

---

---

---

---

---

---

---

## Mass Action Expression

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \text{same for all data sets at equilibrium}$$

Exp't	Equilibrium Concentrations (M)			$Q = \frac{[HI]^2}{[H_2][I_2]}$
	$[H_2]$	$[I_2]$	$[HI]$	
I	0.0222	0.0222	0.156	$\frac{(0.156)^2}{(0.0222)(0.0222)} = 49.4$
II	0.0350	0.0450	0.280	$\frac{(0.280)^2}{(0.0350)(0.0450)} = 49.8$
III	0.0150	0.0135	0.100	$\frac{(0.100)^2}{(0.0150)(0.0135)} = 49.4$
IV	0.0442	0.0442	0.311	$\frac{(0.311)^2}{(0.0442)(0.0442)} = 49.5$
Average = 49.5				

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

362

---

---

---

---

---

---

---

---

## Equilibrium Law

- For reaction at equilibrium write the following

**Equilibrium Law** (at 440 °C)

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 49.5$$

- Equilibrium constant** =  $K_c$  = constant at given T
- Use  $K_c$  since usually working with concentrations in **mol/L**
- For chemical **equilibrium** to exist in reaction mixture, reaction quotient **Q must be equal to** equilibrium constant,  $K_c$

$$Q = K_c$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

363

---

---

---

---

---

---

---

---

## Predicting Equilibrium Law

For general chemical reaction:



- Where **D**, **E**, **F**, and **G** represent chemical formulas
- d**, **e**, **f**, and **g** are coefficients
- Mass action expression =  $\frac{[F]^f [G]^g}{[D]^d [E]^e}$
- Note: Exponents** in mass action expression are **stoichiometric coefficients** in balanced equation.
- Equilibrium law** is:  $K_c = \frac{[F]^f [G]^g}{[D]^d [E]^e}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

364

---

---

---

---

---

---

---

## Ex. Equilibrium Law



- $K_c = 4.26 \times 10^8$  at 25 °C
- What is equilibrium law?

$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]} = 4.26 \times 10^8$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

365

---

---

---

---

---

---

---

## Learning Check

Ex. Write mass action expressions for the following:



$$Q = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$



$$Q = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

366

---

---

---

---

---

---

---

## Manipulating Equations for Chemical Equilibria

Various operations can be performed on equilibrium expressions

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original



$$K_c = \frac{[C][D]}{[A][B]}$$



$$K'_c = \frac{[A][B]}{[C][D]} = \frac{1}{K_c}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

367

---

---

---

---

---

---

---

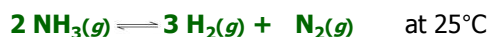
---

## Ex. Manipulating Equilibria 1

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original



$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = 4.26 \times 10^8$$



$$K'_c = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2} = \frac{1}{K_c} = \frac{1}{4.26 \times 10^8} = 2.35 \times 10^{-9}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

368

---

---

---

---

---

---

---

---

## Manipulating Equilibria 2

2. When coefficients in equation are **multiplied by a factor**, equilibrium constant is **raised to a power** equal to that factor.



$$K_c = \frac{[C][D]}{[A][B]}$$



$$K''_c = \frac{[C]^3[D]^3}{[A]^3[B]^3} = \frac{[C][D]}{[A][B]} \times \frac{[C][D]}{[A][B]} \times \frac{[C][D]}{[A][B]} = K_c^3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

369

---

---

---

---

---

---

---

---

## Manipulating Equilibria 2

2. When coefficients in equation are **multiplied by factor**, equilibrium constant is **raised to power** equal to that factor



$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = 4.26 \times 10^8$$

multiply by 3



$$K_c' = \frac{[\text{NH}_3]^6}{[\text{H}_2]^9[\text{N}_2]^3} = K_c^3$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

370

---

---

---

---

---

---

---

---

## Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**



$$K_{c_3} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \times \frac{[\text{F}][\text{G}]}{[\text{C}][\text{E}]} = \frac{[\text{D}][\text{F}][\text{G}]}{[\text{A}][\text{B}][\text{E}]} = K_{c_1} \times K_{c_2}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

371

---

---

---

---

---

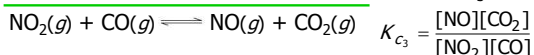
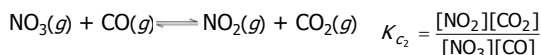
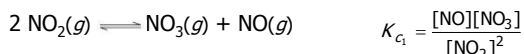
---

---

---

## Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**



$$\frac{[\text{NO}][\text{NO}_3]}{[\text{NO}_2]^2} \times \frac{[\text{NO}_2][\text{CO}_2]}{[\text{NO}_3][\text{CO}]} = \frac{[\text{NO}][\text{CO}_2]}{[\text{NO}_2][\text{CO}]}$$

Therefore

$$K_{c_1} \times K_{c_2} = K_{c_3}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

372

---

---

---

---

---

---

---

---

### Learning Check

Ex.  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$   
 $K_c = 500$  at a particular temperature.

What would be  $K_c$  for following?

- $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$

$$K'_c = \frac{1}{K_c} = \frac{1}{500} = 0.002$$

- $\frac{1}{2} \text{N}_2(g) + \frac{3}{2} \text{H}_2(g) \rightleftharpoons \text{NH}_3(g)$

$$K''_c = K_c^{1/2} = \sqrt{500} = 22.4$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

373

---

---

---

---

---

---

---

---

### Equilibrium Constant, $K_c$

- Constant value equal to ratio of product concentrations to reactant concentrations raised to their respective exponents

$$K_c = \frac{[\text{products}]^f}{[\text{reactants}]^d}$$

- Changes with temperature (van't Hoff Equation)
- Depends on solution concentrations
- Assumes reactants and products are in solution

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

374

---

---

---

---

---

---

---

---

### Equilibrium Constant, $K_p$

- Based on reactions in which substances are gaseous
- Assumes gas quantities are expressed in atmospheres in mass action expression
- Use partial pressures for each gas in place of concentrations
- Ex.  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

375

---

---

---

---

---

---

---

---

## How are $K_p$ and $K_c$ Related?

- Start with Ideal Gas Law

$$PV=nRT$$

- Substituting  $P/RT$  for molar concentration into  $K_c$  results in pressure-based formula
- $\Delta n$  = moles of gas in product – moles of gas in reactant

$$K_p = K_c(RT)^{\Delta n}$$

For gaseous reactions, use either  $K_p$  or  $K_c$

For solution reactions, must use  $K_c$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

376

---

---

---

---

---

---

---

---

## Learning Check

Ex. Consider the reaction:  $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$

If  $K_p = 0.480$  for the reaction at  $25^\circ\text{C}$ , what is value of  $K_c$  at same temperature?

$$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 1 - 2 = -1$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{0.480}{(0.0821 \times 298\text{K})^{-1}}$$

$$K_c = 11.7$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

377

---

---

---

---

---

---

---

---

## Your Turn!

Ex. Consider the reaction  $\text{A}(g) + 2\text{B}(g) \rightleftharpoons 4\text{C}(g)$

If the  $K_c$  for the reaction is 0.99 at  $25^\circ\text{C}$ , what would be the  $K_p$ ?

A. 0.99

B. 2.0

C. 24.

D. 2400

E. None of these

$$\Delta n = (4 - 3) = 1$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 0.99 \times (0.082057 \times 298.15)^1$$

$$K_p = 24$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

378

---

---

---

---

---

---

---

---

### Homogeneous reaction/equilibrium

- All reactants and products in same phase
- Can mix freely

### Heterogeneous reaction/equilibrium

- Reactants and products in different phases
- Can't mix freely
- Solutions are expressed in  $M$
- Gases are expressed in  $M$
- Governed by  $K_c$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

379

---

---

---

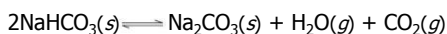
---

---

---

---

### Heterogeneous Equilibria



▪ Equilibrium Law =  $K = \frac{[\text{Na}_2\text{CO}_3(s)][\text{H}_2\text{O}(g)][\text{CO}_2(g)]}{[\text{NaHCO}_3(s)]^2}$

- Can write in simpler form
- For any pure liquid or solid, ratio of moles to volume of substance ( $M$ ) is constant
  - Ex. 1 mol  $\text{NaHCO}_3$  occupies  $38.9 \text{ cm}^3$
  - 2 mol  $\text{NaHCO}_3$  occupies  $77.8 \text{ cm}^3$



$$M = \frac{1 \text{ mol NaHCO}_3}{0.0389 \text{ L}} = 25.7 M$$

$$M = \frac{2 \text{ mol NaHCO}_3}{0.0778 \text{ L}} = 25.7 M$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

380

---

---

---

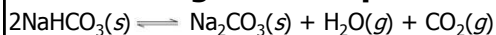
---

---

---

---

### Heterogeneous Equilibria



- concentrations of pure solids and liquids can be incorporated into equilibrium constant,  $K_c$
- Equilibrium law for heterogeneous system written without concentrations of pure solids or liquids

$$K_c = K \frac{[\text{Na}_2\text{CO}_3(s)]}{[\text{NaHCO}_3(s)]^2} = [\text{H}_2\text{O}(g)][\text{CO}_2(g)]$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

381

---

---

---

---

---

---

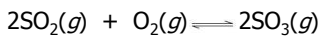
---

### Interpreting $K_c$

#### ▪ Large $K$ ( $K \gg 1$ )

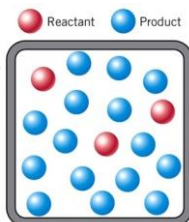
- Means product rich mixture
- Reaction goes far toward completion

Ex.



$$K_c = 7.0 \times 10^{25} \text{ at } 25^\circ \text{C}$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{7.0 \times 10^{25}}{1}$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

382

---

---

---

---

---

---

---

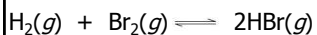
---

### Interpreting $K_c$

#### ▪ Small $K$ ( $K \ll 1$ )

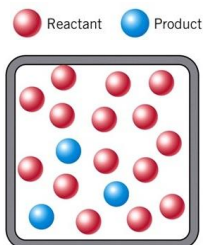
- Means reactant rich mixture
- Only very small amounts of product formed

Ex.



$$K_c = 1.4 \times 10^{-21} \text{ at } 25^\circ \text{C}$$

$$K_c = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]} = \frac{1.4 \times 10^{-21}}{1}$$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

383

---

---

---

---

---

---

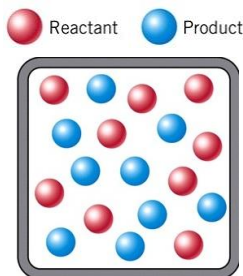
---

---

### Interpreting $K_c$

#### ▪ $K \approx 1$

- Means product and reactant concentrations close to equal
- Reaction goes only  $\sim$  halfway



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

384

---

---

---

---

---

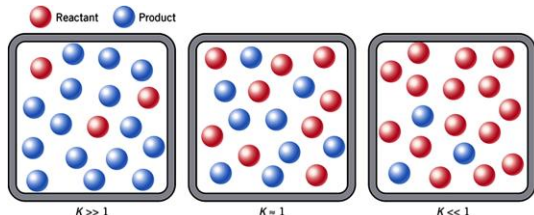
---

---

---



- Size of  $K$  gives measure of how reaction proceeds



- $K \gg 1$  [products]  $\gg$  [reactants]
- $K = 1$  [products] = [reactants]
- $K \ll 1$  [products]  $\ll$  [reactants]

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

385

---

---

---

---

---

---

---

---

## Learning Check

Ex. Consider the reaction of  $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$

If  $K_p = 0.480$  at  $25^\circ\text{C}$ , does the reaction favor product or reactant?

$K$  is small ( $K < 1$ )

Reaction favors **reactant**

Since  $K$  is close to 1, significant amounts of **both** reactant and product are present

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

386

---

---

---

---

---

---

---

---

## Equilibrium Positions and "Shifts"

### Equilibrium positions

- Combination of concentrations that allow  $Q = K$
- Infinite number of possible equilibrium positions

### Le Châtelier's principle

- System at equilibrium ( $Q = K$ ) when upset by disturbance ( $Q \neq K$ ) will shift to offset stress
  - System said to "**shift to right**" when **forward** reaction is dominant ( $Q < K$ )
  - System said to "**shift to left**" when **reverse** direction is dominant ( $Q > K$ )

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

387

---

---

---

---

---

---

---

---

## Relationship Between Q and K

- $Q = K$                       reaction at equilibrium
- $Q < K$                       reactants  $\rightarrow$  products
  - Too many reactants
  - Must convert some reactant to product to move reaction toward equilibrium
- $Q > K$                       reactants  $\leftarrow$  products
  - Too many products
  - Must convert some product to reactant to move reaction toward equilibrium

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

388

---

---

---

---

---

---

---

## Examples of Le Châtelier's Principle

Let's see how this works with changes in

1. Concentration
2. Pressure and volume
3. Temperature
4. Catalysts
5. Adding inert gas to system at constant volume

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

389

---

---

---

---

---

---

---

## Effect of Change in Concentration

- Ex.  $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$
- $K_c = 2.4 \times 10^{-3}$  at 700 °C
- Which direction will the reaction move if 0.125 moles of  $\text{O}_2$  is added to an equilibrium mixture ?
- A. Towards the products
- B. Towards the reactants
- C. No change will occur

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

390

---

---

---

---

---

---

---

## Effect of Change in Concentration

- When changing concentrations of reactants or products
  - Equilibrium shifts to **remove** reactants or products that have been **added**
  - Equilibrium shifts to **replace** reactants or products that have been **removed**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

391

---

---

---

---

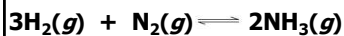
---

---

---

## Effect of Pressure and Volume Changes

Ex. Consider gaseous system at constant **T** and **n**



$$K_P = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

- If reduce volume (**V↓**)
  - Expect Pressure to increase (**P↑**)
  - To reduce pressure, look at each side of reaction
  - Which has less moles of gas
  - Reactants = 3 + 1 = 4 moles gas
  - Products = 2 moles gas
  - Reaction favors products (shifts to right)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

392

---

---

---

---

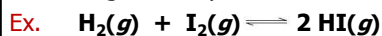
---

---

---

## Effect of P and V Changes

Consider gaseous system at constant **T** and **n**



$$K_P = \frac{P_{\text{HI}}^2}{P_{\text{H}_2} P_{\text{I}_2}}$$

- If pressure is increased, what is the effect on equilibrium?
  - $n_{\text{reactant}} = 1 + 1 = 2$
  - $n_{\text{product}} = 2$
  - Predict no change or shift in equilibrium

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

393

---

---

---

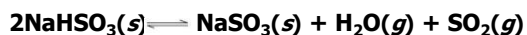
---

---

---

---

## Effect of P and V Changes



$$K_P = P_{\text{H}_2\text{O}} P_{\text{SO}_2}$$

- If you decrease volume of reaction, what is the effect on equilibrium?
  - Reactants: no moles gas = all solids
  - Products: 2 moles gas
  - $\downarrow V$ , causes  $\uparrow P$
  - Reaction shifts to left (reactants), as this has fewer moles of gas

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

394

---

---

---

---

---

---

---

---

## Effect of P and V Changes

- Reducing volume of gaseous reaction mixture causes reaction to decrease number of molecules of gas, if it can
  - Increasing pressure
- Moderate pressure changes have negligible effect on reactions involving only liquids and/or solids
  - Substances are already almost incompressible
- Changes in  $V$ ,  $P$  and  $[X]$  effect position of equilibrium ( $Q$ ), but not  $K$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

395

---

---

---

---

---

---

---

---

## Effect of Temperature Changes



- Energy +  $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$



- Energy is reactant
- Add heat, shift reaction right



- $3 \text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2 \text{NH}_3(g) + \text{energy}$



- Energy is product
- Add heat, shift reaction left

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

396

---

---

---

---

---

---

---

---

## Effect of Temperature Changes

- $\uparrow T$  shifts reaction in direction that produces **endothermic** (heat absorbing) change
- $\downarrow T$  shifts reaction in direction that produces **exothermic** (heat releasing) change
- Changes in  $T$  change value of mass action expression at equilibrium, so  $K$  changed
  - $K$  depends on  $T$
  - $\uparrow T$  of exothermic reaction makes  $K$  smaller
    - More heat (product) forces equilibrium to reactants
  - $\uparrow T$  of endothermic reaction makes  $K$  larger
    - More heat (reactant) forces equilibrium to products

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

397

---

---

---

---

---

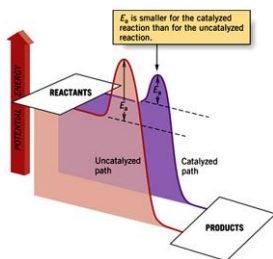
---

---

---

## Catalysts And Equilibrium

- Catalyst lowers  $E_a$  for both forward and reverse reaction
- Change in  $E_a$  affects rates  $k_f$  and  $k_r$  equally
- Catalysts have no effect on equilibrium



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

398

---

---

---

---

---

---

---

---

## Effect of Adding Inert Gas

### Inert gas

- One that does not react with components of reaction
- Ex.** Argon, Helium, Neon, usually  $N_2$
- Adding inert gas to reaction at fixed  $V$  ( $n$  and  $T$ ),  $\uparrow P$  of all reactants and products
- Since it doesn't react with anything
  - No change in concentrations of reactants or products
  - No net effect on reaction

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

399

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** The following are equilibrium constants for the reaction of acids in water,  $K_a$ . Which is the most acid dissociated reaction?

- A.  $K_a = 2.2 \times 10^{-3}$
- B.  $K_a = 1.8 \times 10^{-5}$
- C.  $K_a = 4.0 \times 10^{-10}$
- D.  $K_a = 6.3 \times 10^{-3}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

400

---

---

---

---

---

---

---

---

## Calculating $K_c$ Given Equilibrium Concentrations

**Ex.**  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

- If you place 0.0350 mol  $\text{N}_2\text{O}_4$  in 1 L flask at equilibrium, what is  $K_c$ ?
- $[\text{N}_2\text{O}_4]_{\text{eq}} = 0.0292 \text{ M}$
- $[\text{NO}_2]_{\text{eq}} = 0.0116 \text{ M}$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \quad K_c = \frac{[0.0116]^2}{[0.0292]}$$

$$K_c = 4.61 \times 10^{-3}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

401

---

---

---

---

---

---

---

---

## Your Turn!

**Ex.** For the reaction:  $2\text{A}(aq) + \text{B}(aq) \rightleftharpoons 3\text{C}(aq)$  the equilibrium concentrations are:  $\text{A} = 2.0 \text{ M}$ ,  $\text{B} = 1.0 \text{ M}$  and  $\text{C} = 3.0 \text{ M}$ . What is the expected value of  $K_c$  at this temperature?

- A. 14
- B. 0.15
- C. 1.5
- D. 6.75

$$K_c = \frac{[\text{C}]^3}{[\text{A}]^2[\text{B}]}$$

$$K_c = \frac{[3.0]^3}{[2.0]^2[1.0]}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

402

---

---

---

---

---

---

---

---

### Calculating $K_c$ Given Initial Concentrations and One Final Concentration



- 1.000 mol  $\text{SO}_2$  and 1.000 mol  $\text{O}_2$  are placed in a 1.000 L flask at 1000 K. At equilibrium 0.925 mol  $\text{SO}_3$  has formed. Calculate  $K_c$  for this reaction.

- 1<sup>st</sup> calculate concentrations of each

- Initial  $[\text{SO}_2] = [\text{O}_2] = \frac{1.00 \text{ mol}}{1.00 \text{ L}} = 1.00 \text{ M}$

- Equilibrium  $[\text{SO}_3] = \frac{0.925 \text{ mol}}{1.00 \text{ L}} = 0.925 \text{ M}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

403

### Set up Concentration Table

	$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$		
Initial Conc. (M)	1.000	1.000	0.000
Changes in Conc. (M)	-0.925	-0.462	+0.925
Equilibrium Conc. (M)	0.075	0.538	0.925

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

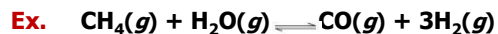
$$K_c = \frac{[0.925]^2}{[0.075]^2[0.538]} \quad K_c = 2.8 \times 10^2 = 280$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

404

### Calculate $[X]_{\text{equilibrium}}$ from $K_c$ and $[X]_{\text{initial}}$



- At 1500 °C,  $K_c = 5.67$ . An equilibrium mixture of gases had the following concentrations:  $[\text{CH}_4] = 0.400 \text{ M}$  and  $[\text{H}_2] = 0.800 \text{ M}$  and  $[\text{CO}] = 0.300 \text{ M}$ . What is  $[\text{H}_2\text{O}]$  at equilibrium ?

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

405

### Calculate $[X]_{\text{equilibrium}}$ from $K_c$ and $[X]_{\text{initial}}$

**Ex.**  $\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g)$   $K_c = 5.67$

$[\text{CH}_4] = 0.400 \text{ M}$ ;  $[\text{H}_2] = 0.800 \text{ M}$ ;  $[\text{CO}] = 0.300 \text{ M}$

- What is  $[\text{H}_2\text{O}]$  at equilibrium?

- First, set up equilibrium

$$K_c = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4][\text{H}_2\text{O}]} \quad [\text{H}_2\text{O}] = \frac{[\text{CO}][\text{H}_2]^3}{[\text{CH}_4]K_c}$$

- Next, plug in equilibrium concentrations and  $K_c$

$$[\text{H}_2\text{O}] = \frac{[0.300][0.800]^3}{[0.400](5.67)} = \frac{0.154}{2.27}$$

**$[\text{H}_2\text{O}] = 0.0678 \text{ M}$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

406

---

---

---

---

---

---

---

---

### Calculate $[X]_{\text{equilibrium}}$ from $[X]_{\text{initial}}$ and $K_c$

**Ex.**  $\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)$  at  $425^\circ\text{C}$

$K_c = 55.64$

- If one mole each of  $\text{H}_2$  and  $\text{I}_2$  are placed in a  $0.500 \text{ L}$  flask at  $425^\circ\text{C}$ , what are the equilibrium concentrations of  $\text{H}_2$ ,  $\text{I}_2$  and  $\text{HI}$ ?

- Step 1. Write Equilibrium Law**

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = 55.64$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

407

---

---

---

---

---

---

---

---

### **Ex. Step 2. Concentration Table**

Conc (M)	$\text{H}_2(g)$	+	$\text{I}_2(g)$	$\rightleftharpoons$	$2\text{HI}(g)$
Initial	2.00		2.00		0.000
Change	$-x$		$-x$		$+2x$
Equil'm	$2.00 - x$		$2.00 - x$		$+2x$

- Initial  $[\text{H}_2] = [\text{I}_2] = 1.00 \text{ mol}/0.500 \text{ L} = 2.00 \text{ M}$
- Amt of  $\text{H}_2$  consumed = Amt of  $\text{I}_2$  consumed =  $x$
- Amt of  $\text{HI}$  formed =  $2x$

$$55.64 = \frac{(2x)^2}{(2.00 - x)(2.00 - x)} = \frac{(2x)^2}{(2.00 - x)^2}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

408

---

---

---

---

---

---

---

---



### Ex. Step 3. Solve for x

- Both sides are squared so we can take square root of both sides to simplify

$$\sqrt{K} = \sqrt{55.64} = \sqrt{\frac{(2x)^2}{(2.00 - x)^2}}$$

$$7.459 = \frac{2x}{(2.00 - x)} \quad 7.459(2.00 - x) = 2x$$

$$14.918 - 7.459x = 2x \quad 14.918 = 9.459x$$

$$x = \frac{14.918}{9.459} = 1.58$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

409

---

---

---

---

---

---

---

### Ex. Step 4. Equilibrium Concentrations

Conc (M)	H <sub>2</sub> (g)	+	I <sub>2</sub> (g)	⇌	2HI(g)
Initial	2.00		2.00		0.00
Change	-1.58		-1.58		+3.16
Equil'm	0.42		0.42		+3.16

- [H<sub>2</sub>]<sub>equil</sub> = [I<sub>2</sub>]<sub>equil</sub> = 2.00 - 1.58 = 0.42 M
- [HI]<sub>equil</sub> = 2x = 2(1.58) = 3.16

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

410

---

---

---

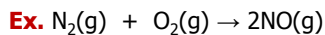
---

---

---

---

### Your Turn!



$$K_c = 0.0123 \text{ at } 3900^\circ\text{C}$$

If 0.25 moles of N<sub>2</sub> and O<sub>2</sub> are placed in a 250 mL container, what are the equilibrium concentrations of all species?

- A. 0.0526 M, 0.947 M, 0.105 M
- B. 0.947 M, 0.947 M, 0.105 M
- C. 0.947 M, 0.105 M, 0.0526 M
- D. 0.105 M, 0.105 M, 0.947 M

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

411

---

---

---

---

---

---

---

## Your Turn! - Solution

**Ex.** Conc (M)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

Initial	1.00	1.00	0.00
Change	$-x$	$-x$	$+2x$
Equil	$1.00 - x$	$1.00 - x$	$+2x$

$$[\text{N}_2] = [\text{O}_2] = \frac{0.250 \text{ mol}}{0.250 \text{ L}} = 1.00 \text{ M}$$

$$0.0123 = \frac{(2x)^2}{(1-x)^2} \quad \sqrt{0.0123} = \frac{2x}{1-x}$$

$$x = 0.0526 \text{ M} \quad [\text{NO}] = 2x = 0.105 \text{ M}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

412

## Learning Check

**EX.** For the reaction  $2\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$

given that  $K_p = 3.5 \times 10^{-16}$  at  $25^\circ\text{C}$ , and we place 0.2 atm A into the container, what will be the pressure of B at equilibrium?

	<b>2A</b>	$\leftrightarrow$	<b>B</b>
I	0.2		0 atm
C	$-2x$		$+x$
E	$0.2 - 2x$		$x$

$$3.5 \times 10^{-16} = \frac{x}{(0.2)^2} \quad x = 1.4 \times 10^{-17} \quad [\text{B}] = 1.4 \times 10^{-17} \text{ M}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

413

## Calculating $K_C$ Given Initial Concentrations and One Final Concentration

**Ex.**  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  @  $450^\circ\text{C}$

- Initially  $\text{H}_2$  and  $\text{I}_2$  concentrations are 0.200 mol each in 2.00 L. At equilibrium, HI concentration is 0.160 M. Calculate  $K_C$

$$[\text{I}_2] = [\text{H}_2] = 0.100 \text{ M}$$

$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$	@ $450^\circ\text{C}$
0.100M		0.100M		0	
$-x$		$-x$		$2x$	
$0.100-x$		$0.100-x$		$2x$	
				$2x=0.160$	

- $x = 0.08 \text{ M}$
- $[\text{I}_2] = [\text{H}_2] = 0.100 - 0.08 = 0.020 \text{ M}$
- $K_C = (0.160)^2 / (0.020)^2 = 64$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

414

## Chapter 7

### Acids and Bases

Chemistry: The Molecular Nature  
of Matter, 6E

Jespersen/Brady/Hyslop



---

---

---

---

---

---

---

### Arrhenius Acids and Bases

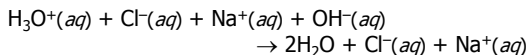
**Acid** produces  $\text{H}_3\text{O}^+$  in water

**Base** gives  $\text{OH}^-$

#### Acid-base neutralization

- Acid and base combine to produce water and a salt.

Ex.  $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{H}_2\text{O} + \text{NaCl}(aq)$



- Many reactions resemble this without forming  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  in solution

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

416

---

---

---

---

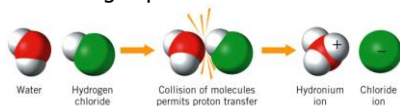
---

---

---

### Brønsted-Lowry Definition

- Acid** = proton donor
- Base** = proton acceptor
- Allows for gas phase acid-base reactions



Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Ex.  $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$

- HCl** = **acid**
  - Donates  $\text{H}^+$
- Water** = **base**
  - Accepts  $\text{H}^+$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

417

---

---

---

---

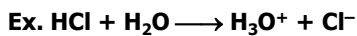
---

---

---

## Conjugate Acid-Base Pair

- Species that differ by  $\text{H}^+$



- $\text{HCl} = \text{acid}$
- Water = base**
- $\text{H}_3\text{O}^+$ 
  - Conjugate acid of  $\text{H}_2\text{O}$
- $\text{Cl}^-$ 
  - Conjugate base of  $\text{HCl}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

418

---

---

---

---

---

---

---

---

## Formic Acid is Bronsted Acid

- Formic acid ( $\text{HCHO}_2$ ) is a weak acid
- Must consider equilibrium
  - $\text{HCHO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{CHO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- Focus on forward reaction



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

419

---

---

---

---

---

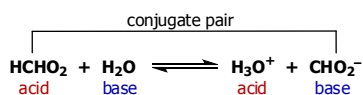
---

---

---

## Formate Ion is Bronsted Base

- Now consider reverse reaction
- Hydronium ion transfers  $\text{H}^+$  to  $\text{CHO}_2^-$



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

420

---

---

---

---

---

---

---

---

## Learning Check

- Identify the Conjugate Partner for Each

conjugate base	conjugate acid
$\text{Cl}^-$	$\text{HCl}$
$\text{NH}_3$	$\text{NH}_4^+$
$\text{C}_2\text{H}_3\text{O}_2^-$	$\text{HC}_2\text{H}_3\text{O}_2$
$\text{CN}^-$	$\text{HCN}$
$\text{F}^-$	$\text{HF}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

421

---

---

---

---

---

---

---

---

## Learning Check

- Write a reaction that shows that  $\text{HCO}_3^-$  is a Brønsted **acid** when reacted with  $\text{OH}^-$
- $\text{HCO}_3^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{H}_2\text{O}(\ell) + \text{CO}_3^{2-}(aq)$
- Write a reaction that shows that  $\text{HCO}_3^-$  is a Brønsted **base** when reacted with  $\text{H}_3\text{O}^+(aq)$
- $\text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(\ell)$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

422

---

---

---

---

---

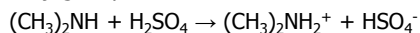
---

---

---

## Your Turn!

**Ex.** In the following reaction, identify the acid/base conjugate pair.



- A.  $(\text{CH}_3)_2\text{NH} / \text{H}_2\text{SO}_4$  ;  $(\text{CH}_3)_2\text{NH}^+ / \text{HSO}_4^-$
- B.  $(\text{CH}_3)_2\text{NH} / (\text{CH}_3)_2\text{N}^{+2}$  ;  $\text{H}_2\text{SO}_4 / \text{SO}_4^{2-}$
- C.  $\text{H}_2\text{SO}_4 / \text{HSO}_4^-$  ;  $(\text{CH}_3)_2\text{NH}_2^+ / (\text{CH}_3)_2\text{NH}$
- D.  $\text{H}_2\text{SO}_4 / (\text{CH}_3)_2\text{NH}$  ;  $(\text{CH}_3)_2\text{NH}^+ / \text{HSO}_4^-$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

423

---

---

---

---

---

---

---

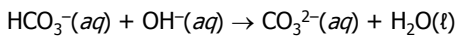
---

## Amphoteric Substances

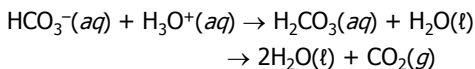
- Can act as either **acid** or **base**
  - Also called **amphiprotic**
  - Can be either molecules or ions

**Ex.** hydrogen carbonate ion:

- Acid:**



- Base:**



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

424

---

---

---

---

---

---

---

## Your Turn!

**Ex.** Which of the following can act as an amphoteric substance?

- A.  $\text{CH}_3\text{COOH}$
- B.  $\text{HCl}$
- C.  $\text{NO}_2^-$
- D.  $\text{HPO}_4^{2-}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

425

---

---

---

---

---

---

---

## Strengths of Acids and Bases

### Strength of Acid

- Measure of its ability to transfer  $\text{H}^+$
- Strong acids**
  - React completely with water **Ex.**  $\text{HCl}$  and  $\text{HNO}_3$
- Weak acids**
  - Less than completely ionized **Ex.**  $\text{CH}_3\text{COOH}$  and  $\text{CHOOH}$

**Strength of Base** classified in similar fashion:

- Strong bases**
    - React completely with water **Ex.** Oxide ion ( $\text{O}^{2-}$ ) and  $\text{OH}^-$
  - Weak bases**
    - Undergo incomplete reactions
- Ex.**  $\text{NH}_3$  and  $\text{NRH}_2$  ( $\text{NH}_2\text{CH}_3$ , methylamine)

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

426

---

---

---

---

---

---

---

## Reactions of Strong Acids and Bases

### In water

- **Strongest acid** = hydronium ion,  $\text{H}_3\text{O}^+$ 
  - If more powerful  $\text{H}^+$  donor added to  $\text{H}_2\text{O}$
  - Reacts with  $\text{H}_2\text{O}$  to produce  $\text{H}_3\text{O}^+$

Similarly,

- **Strongest base** is hydroxide ion ( $\text{OH}^-$ )
  - More powerful  $\text{H}^+$  acceptors
  - React with  $\text{H}_2\text{O}$  to produce  $\text{OH}^-$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

427

---

---

---

---

---

---

---

## Position of Acid-Base Equilibrium

- Acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) is **weak acid**
  - Ionizes only slightly in water



- Hydronium ion
  - **Better**  $\text{H}^+$  donor than acetic acid
  - **Stronger acid**
- Acetate ion
  - **Better**  $\text{H}^+$  acceptor than water
  - **Stronger base**
- Position of equilibrium **favours weaker** acid and base

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

428

---

---

---

---

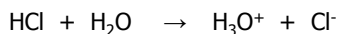
---

---

---

## Your Turn!

**Ex.** In the reaction:



which species is the weakest base ?

- A.  $\text{HCl}$
- B.  $\text{H}_2\text{O}$
- C.  $\text{H}_3\text{O}^+$
- D.  $\text{Cl}^-$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

429

---

---

---

---

---

---

---

### In General

- **Stronger** acids and bases tend to react with each other to produce their **weaker** conjugates
- **Stronger** Brønsted acid has **weaker** conjugate base
- **Weaker** Brønsted acid has **stronger** conjugate base

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

430

---

---

---

---

---

---

---

---

### Autoionization of water

- Trace ionization  $\equiv$  self-ionization of water
- $\text{H}_2\text{O}(\ell) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$   
acid      base      acid      base
- Equilibrium law is:  $K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$
- But  $[\text{H}_2\text{O}]_{\text{pure}} = \frac{1000 \text{ g}}{18.0 \text{ g/mol}} = 55.6 \text{ M}$   
1.00L
- $[\text{H}_2\text{O}] = \text{constant}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

431

---

---

---

---

---

---

---

---

### Autoionization of water



- Since  $\therefore [\text{H}_2\text{O}] = \text{constant}$
- Equilibrium law simplifies to

$$K_c \times [\text{H}_2\text{O}]^2 = [\text{H}^+][\text{OH}^-] = K_w$$

- Where  $K_w$  = ion product constant for water
- Often omit 2<sup>nd</sup> H<sub>2</sub>O molecule and write
- $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_w = [\text{H}^+][\text{OH}^-]$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

432

---

---

---

---

---

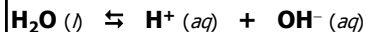
---

---

---



### Autoionization of water



- for pure  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$
- $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$
- $K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = \mathbf{1.0 \times 10^{-14}}$

$\text{H}_2\text{O}$  auto-ionization occurs in any solution

- $K_w = [\text{H}^+][\text{OH}^-] = \mathbf{1.0 \times 10^{-14}}$  at  $25^\circ\text{C}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

433

---

---

---

---

---

---

---

---

### Self-Ionization of Water

- In aqueous solution,
- **Product of  $[\text{H}^+]$  and  $[\text{OH}^-]$  equals  $K_w$**
- **$[\text{H}^+]$  and  $[\text{OH}^-]$**  may not actually equal each other

#### Solution Classification

Neutral	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$
Acidic	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$
Basic	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

434

---

---

---

---

---

---

---

---

### Learning Check

**Ex.** In a sample of blood at  $25^\circ\text{C}$ ,  $[\text{H}^+] = 4.6 \times 10^{-8} M$ . Find  $[\text{OH}^-]$  and determine if the solution is acidic, basic or neutral.

$$K_w = [\text{H}^+][\text{OH}^-] = \mathbf{1 \times 10^{-14}}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{\mathbf{1.0 \times 10^{-14}}}{4.6 \times 10^{-8}} = \mathbf{2.2 \times 10^{-7}}$$

- So  $2.2 \times 10^{-7} M > 4.6 \times 10^{-8} M$
- $[\text{OH}^-] > [\text{H}_3\text{O}^+]$
- Solution slightly **basic**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

435

---

---

---

---

---

---

---

---

## The pH Concept

- In general

$$\text{pH} = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$\text{pX} = -\log X$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{p}K_w = -\log K_w = 14.00$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

436

---

---

---

---

---

---

---

## Using Logarithms

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$-\log([\text{H}^+][\text{OH}^-]) = -\log K_w = -\log(1.0 \times 10^{-14})$$

$$-\log[\text{H}^+] - \log[\text{OH}^-] = -\log K_w = -(-14.00)$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

437

---

---

---

---

---

---

---

## Redefine Acidic, Basic and Neutral Solutions in terms of pH!

- As **pH** ↑, **[H<sup>+</sup>]** ↓; **pOH** ↓, and **[OH<sup>-</sup>]** ↑
- As **pH** ↓, **[H<sup>+</sup>]** ↑; **pOH** ↑, and **[OH<sup>-</sup>]** ↓

Neutral	pH = 7.00
Acidic	pH < 7.00
Basic	pH > 7.00

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

438

---

---

---

---

---

---

---

## Your Turn!

**Ex.**  $K_w$  increases with increasing temperature. At 50 °C,  $K_w = 5.476 \times 10^{-14}$ . What is the pH of a neutral solution at 50 °C ?

- A. 7.00
- B. 6.63
- C. 7.37
- D. 15.3

$$[H^+] = [OH^-] = (5.476 \times 10^{-14})^{1/2} = 2.34 \times 10^{-7}$$

$$pH = -\log[H^+] = -\log 2.34 \times 10^{-7} = 6.63$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

439

---

---

---

---

---

---

---

---

## Learning Check

**Ex.** What are  $[H^+]$  and  $[OH^-]$  of **pH = 3.00** solution?

- $[H^+] = 10^{-3.00} = 1.0 \times 10^{-3} M$

- $[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11} M$

**Ex.** What are  $[H^+]$  and  $[OH^-]$  of **pH = 4.00** solution?

- **pH = 4.00**     $[H^+] = 1.0 \times 10^{-4} M$

- $[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$

- **Or** **pH 4.00** solution has 10 times less  $H^+$  than **pH 3.00** solution

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

440

---

---

---

---

---

---

---

---

## Sample pH Calculations

**Ex.** Calculate pH and pOH of blood where

$$[H^+] = 4.6 \times 10^{-8} M$$

$$[OH^-] = 2.2 \times 10^{-7} M$$

$$pH = -\log(4.6 \times 10^{-8}) = 7.34$$

$$pOH = -\log(2.2 \times 10^{-7}) = 6.66$$

$$14.00 = pK_w$$

**or**

$$pOH = 14.00 - pH = 14.00 - 7.34 = 6.66$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

441

---

---

---

---

---

---

---

---

### Sample pH Calculations (cont'd)

**Ex.** What is the pH of NaOH solution at 25 °C in which the OH<sup>-</sup> concentration is 0.0026 *M*?

- [OH<sup>-</sup>] = 0.0026 *M*
- pOH = -log(0.0026) = 2.59
- pH = 14.00 – pOH
- = 14.00 – 2.59
- = **11.41**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

442

---

---

---

---

---

---

---

### Your Turn!

**Ex.** A sample of juice has a pH of 3.76. Calculate [H<sup>+</sup>].

A.  $7.6 \times 10^{-3} \text{ M}$

B. 3.76 *M*

C. 10.24 *M*

D.  $5.9 \times 10^{-9} \text{ M}$

E.  $1.7 \times 10^{-4} \text{ M}$

$$\begin{aligned} [\text{H}^+] &= 10^{-\text{pH}} \\ &= 10^{-3.76} \\ &= \mathbf{1.7 \times 10^{-4} \text{ M}} \end{aligned}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

443

---

---

---

---

---

---

---

### Learning Check

**Ex.** What is the [H<sub>3</sub>O<sup>+</sup>] and pH of a solution that has [OH<sup>-</sup>] =  $3.2 \times 10^{-3} \text{ M}$ ?

- [H<sub>3</sub>O<sup>+</sup>][OH<sup>-</sup>] =  $1 \times 10^{-14}$
- [H<sub>3</sub>O<sup>+</sup>] =  $1 \times 10^{-14} / 3.2 \times 10^{-3} = 3.1 \times 10^{-12} \text{ M}$
- pH = -log [H<sub>3</sub>O<sup>+</sup>] = -log( $3.1 \times 10^{-12}$ ) = 11.50

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

444

---

---

---

---

---

---

---

### Your Turn!

**Ex.** What is the  $[\text{OH}^-]$  and pH of a solution that has  $[\text{H}_3\text{O}^+] = 2.3 \times 10^{-5} \text{ M}$ ?

- |    | $[\text{H}_3\text{O}^+]$        | pH    |
|----|---------------------------------|-------|
| A. | $2.3 \times 10^{-5} \text{ M}$  | 9.40  |
| B. | $1.0 \times 10^{-14} \text{ M}$ | 14.00 |
| C. | $4.3 \times 10^{-10} \text{ M}$ | 4.60  |
| D. | $7.7 \times 10^{-9} \text{ M}$  | 5.23  |
| E. | $1.0 \times 10^{-7} \text{ M}$  | 7.00  |

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

445

---

---

---

---

---

---

---

---

### Learning Check

**Ex.** What is the pOH and the  $[\text{H}_3\text{O}^+]$  of a solution that has a pH of 2.33?

pOH = 11.67

$[\text{H}_3\text{O}^+] = 4.7 \times 10^{-3}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

446

---

---

---

---

---

---

---

---

### Your Turn!

**Ex.** What is the pH and the  $[\text{H}_3\text{O}^+]$  of a solution that has a pOH of 1.89?

- |    | $[\text{H}_3\text{O}^+]$         | pH    |
|----|----------------------------------|-------|
| A. | $1.29 \times 10^{-2} \text{ M}$  | 1.89  |
| B. | $1.0 \times 10^{-14} \text{ M}$  | 14.00 |
| C. | $1.50 \times 10^{-11} \text{ M}$ | 10.82 |
| D. | $7.8 \times 10^{-13} \text{ M}$  | 12.11 |
| E. | $1.0 \times 10^{-7} \text{ M}$   | 7.00  |

pOH = 1.89  
 $[\text{OH}^-] = \text{Shift log } -\text{pOH}$   
 $[\text{OH}^-] = 0.0129$   
 $[\text{H}^+] = 10^{-14} / 0.0129 = 7.8 \times 10^{-13}$   
 $\text{pH} = -\log \text{H}^+ = -\log 7.8 \times 10^{-13}$   
 $\text{pH} = 12.11$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

447

---

---

---

---

---

---

---

---

## Strong Acids: pH of Dilute Solutions

### Strong Acids

- Assume 100% dissociated in solution
  - Good ~ if dilute
- Makes calculating  $[H^+]$  and  $[OH^-]$  easier
- 1 mole  $H^+$  for every 1 mole HA**
  - So  $[H^+] = [HA]$  for strong acids
- Thus, if 0.040 M  $HClO_4$
- $[H^+] = 0.040$  M
- And  **$pH = -\log(0.040) = 1.40$**

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

448

## pH of Dilute Solutions of Strong Bases

### Strong Bases

- |                     |   |  |
|---------------------|---|--|
| NaOH                | } | <ul style="list-style-type: none"> <li>1 mole <math>OH^-</math> for every 1 mole <b>B</b></li> <li><math>[OH^-] = [B]</math> for strong bases</li> </ul>   |
| KOH                 |   |  |
| LiOH                |   |  |
| Ca(OH) <sub>2</sub> | } | <ul style="list-style-type: none"> <li>2 mole <math>OH^-</math> for every 1 mole <b>B</b></li> <li><math>[OH^-] = 2*[B]</math> for strong bases</li> </ul> |
| Ba(OH) <sub>2</sub> |   |  |
| Sr(OH) <sub>2</sub> |   |  |

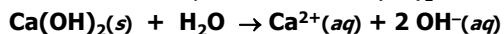
Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

449

## Learning Check

**Ex.** Calculate the pH of 0.011 M  $Ca(OH)_2$ .



- $[OH^-] = 2*[Ca(OH)_2] = 2*0.011M = 0.022M$
- $pOH = -\log(0.022) = 1.66$
- $pH = 14.00 - pOH$
- $= 14.00 - 1.66 = \boxed{12.34}$
- What is this in the  $[H^+]$  of the solution?
- $[H^+] = 10^{-12.34} = 4.6 \times 10^{-13} M$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

450

## Learning Check

### Ex. What is the pH of 0.1M HCl?

- Assume 100% dissociation



I	0.1	N/A	0	0
C	-0.1	-0.1	0.1	0.1
End	0	N/A	0.1	0.1

$$\text{pH} = -\log(0.1) = \mathbf{1}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

451

---

---

---

---

---

---

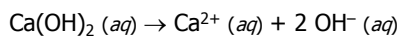
---

---

## Learning Check

### Ex. What is the pH of 0.5M Ca(OH)<sub>2</sub>?

- Assume 100% dissociation



I	0.5	0	0
C	-0.5	+0.5	+0.5×2
E	0	0.5	1.0

$$\text{pOH} = -\log(1.0) = 0$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 0 = \mathbf{14}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

452

---

---

---

---

---

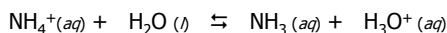
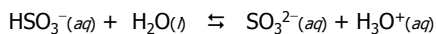
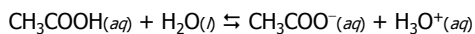
---

---

---

## Weak Acids and Bases

- Incompletely ionized
- Molecules and ions exist in equilibrium
- Reaction of a Weak Acid with Water**



Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

453

---

---

---

---

---

---

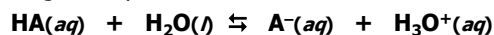
---

---

## Weak Acid/Base Equilibria

Acid + Water  $\rightleftharpoons$  Conjugate Base + Hydronium Ion

Or generally



$$K'_c = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

- But  $[\text{H}_2\text{O}] = \text{constant}$  (55.6 M) so rewrite as

$$K'_c \times [\text{H}_2\text{O}] = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} = K_a$$

- Where  $K_a = \text{acid ionization constant}$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

454

## Weak Acid/Base Equilibria

- Often simplify as



$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]}$$

$$\text{p}K_a = -\log K_a$$

$$K_a = 10^{-\text{p}K_a}$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

455

**Table 17.2 Weak Monoprotic Acids at 25 °C**

Name of Acid	Formula	$K_a$	$\text{p}K_a$
Iodic acid	$\text{HIO}_3$	$1.7 \times 10^{-1}$	0.77
Chloroacetic acid	$\text{HC}_2\text{H}_2\text{O}_2\text{Cl}$	$1.4 \times 10^{-3}$	2.85
Nitrous acid	$\text{HNO}_2$	$4.6 \times 10^{-4}$	3.34
Hydrofluoric acid	$\text{HF}$	$3.5 \times 10^{-4}$	3.46
Cyanic acid	$\text{HOCN}$	$2 \times 10^{-4}$	3.7
Formic acid	$\text{HCHO}_2$	$1.8 \times 10^{-4}$	3.74
Barbituric acid	$\text{HC}_4\text{H}_3\text{N}_2\text{O}_3$	$9.8 \times 10^{-5}$	4.01
Hydrazoic acid	$\text{HN}_3$	$2.5 \times 10^{-5}$	4.60
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	$1.8 \times 10^{-5}$	4.74
Butanoic acid	$\text{HC}_4\text{H}_7\text{O}_2$	$1.5 \times 10^{-5}$	4.82
Propanoic acid	$\text{HC}_3\text{H}_5\text{O}_2$	$1.3 \times 10^{-5}$	4.89
Hypochlorous acid	$\text{HOCl}$	$3.0 \times 10^{-8}$	7.52
Hydrocyanic acid	$\text{HCN}$	$4.9 \times 10^{-10}$	9.31
Phenol	$\text{HC}_6\text{H}_5\text{O}$	$1.3 \times 10^{-10}$	9.89
Hydrogen peroxide	$\text{H}_2\text{O}_2$	$2.4 \times 10^{-12}$	11.62

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

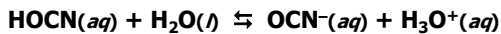
Chemistry: The Molecular Nature of Matter, 6E

456



### Learning Check

**Ex.** What is the  $pK_a$  of HOAC if  $K_a = 3.5 \times 10^{-4}$ ?



or



$$K_a = \frac{[\text{OCN}^-][\text{H}^+]}{[\text{HOCN}]} = 3.5 \times 10^{-4}$$

$$pK_a = -\log K_a = -\log(3.5 \times 10^{-4}) = \mathbf{3.46}$$

---

---

---

---

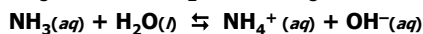
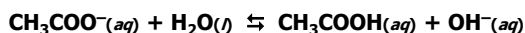
---

---

---

---

### Reaction of a Weak Base with Water



▪ Or generally



$$K'_c = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]} \quad \text{But } [\text{H}_2\text{O}] = \text{constant}$$

so can rewrite as

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \quad \text{Where } K_b = \text{base ionization constant}$$

$$pK_b = -\log K_b \quad K_b = 10^{-pK_b}$$

---

---

---

---

---

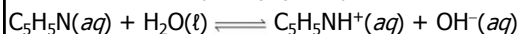
---

---

---

### Learning Check

**Ex.** What is the  $pK_b$  of  $\text{C}_5\text{H}_5\text{N}$  if  $K_a = 3.5 \times 10^{-4}$ ?



$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = 1.7 \times 10^{-9}$$

$$pK_b = -\log K_b = -\log(1.7 \times 10^{-9}) = \mathbf{8.76}$$

---

---

---

---

---

---

---

---

**Table 17.3 Weak Bases at 25 °C**

Table 17.3 $K_b$ and $pK_b$ Values for Weak Molecular Bases at 25 °C			
Name of Base	Formula	$K_b$	$pK_b$
Butylamine	$C_4H_9NH_2$	$5.9 \times 10^{-4}$	3.23
Methylamine	$CH_3NH_2$	$4.4 \times 10^{-4}$	3.36
Ammonia	$NH_3$	$1.8 \times 10^{-5}$	4.74
Strychnine	$C_{21}H_{22}N_2O_2$	$1.8 \times 10^{-6}$	5.74
Morphine	$C_{17}H_{19}NO_3$	$1.6 \times 10^{-6}$	5.80
Hydrazine	$N_2H_4$	$1.3 \times 10^{-6}$	5.89
Hydroxylamine	$HONH_2$	$1.1 \times 10^{-8}$	7.96
Pyridine	$C_5H_5N$	$1.7 \times 10^{-9}$	8.87
Aniline	$C_6H_5NH_2$	$3.9 \times 10^{-10}$	9.41

Copyright © 2012 John Wiley & Sons, Inc. All rights reserved.

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

460

### Conjugate Acid-Base Pairs and Values of $K_a$ and $K_b$

$$K_a \times K_b = \frac{[A^-][H^+]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H^+][OH^-] = K_w$$

For any conjugate acid base pair:

$$K_a \times K_b = K_w = 1.0 \times 10^{-14} \quad (\text{at } 25^\circ\text{C})$$

$$pK_a + pK_b = pK_w = 14.00$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

461

**Ex.** Nicotinic acid (niacin) is a monoprotic acid with the formula  $HC_6H_4NO_2$ . A solution that is 0.012 *M* in nicotinic acid has a pH of 3.39 at 25 °C. What are the acid-ionization constant,  $K_a$ , and  $pK_a$  for this acid at 25 °C? What is the degree of ionization of nicotinic acid in this solution? Let **HNic** = nicotinic acid and **Nic<sup>-</sup>** = anion.

$$HNic(aq) + H_2O(l) \rightleftharpoons Nic^-(aq) + H_3O^+(aq)$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

462

### Ex. (cont)

$$K_a = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]}$$

	[HNic] (M)	[Nic <sup>-</sup> ] (M)	[H <sub>3</sub> O <sup>+</sup> ] (M)
<b>I</b>	0.012	0	0
<b>C</b>	-x	+x	+x
<b>E</b>	0.012 - x	x	x

What is value of x?

- Only source of H<sup>+</sup> is ionization of **HNic**, then can get x from [H<sup>+</sup>]
- x = antilog(-pH) = 10<sup>-pH</sup> = 10<sup>-3.39</sup>  
= **4.1 x 10<sup>-4</sup>** = [H<sup>+</sup>]

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

463

### Ex. (cont)

- Since **Nic<sup>-</sup>** is formed in **1:1** ratio with **H<sup>+</sup>**, then
  - [**Nic<sup>-</sup>**] = x = 4.1 x 10<sup>-4</sup>
- Finally only reason **HNic** disappears is because it ionizes, so loss of [**HNic**] = -x

$$K_a = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]} = \frac{x * x}{0.012 - x} = \frac{x^2}{0.012 - x}$$

- But we know [**Nic<sup>-</sup>**], so can put into concentration table and solve for each

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

464

### Ex. (cont)

$$K_a = \frac{[\text{Nic}^-][\text{H}^+]}{[\text{HNic}]}$$

	[HNic] (M)	[Nic <sup>-</sup> ] (M)	[H <sup>+</sup> ] (M)
<b>I</b>	0.0120	0	0
<b>C</b>	- 0.00041	+ 0.00041	+ 0.00041
<b>E</b>	0.0120 - 0.00041 = 0.01159 <b>≈ 0.012</b>	<b>0.00041</b>	<b>0.00041</b>

- Notice if **c** >> **K<sub>a</sub>**, then equilibrium concentration of acid is approximated as initial concentration

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

465

### Ex. (cont)

- Now ready to calculate  $K_a$ .

$$K_a = \frac{x^2}{0.012 - x} \approx \frac{x^2}{0.012} = \frac{(0.00041)^2}{0.012} = 1.4 \times 10^{-5}$$

$$\text{p}K_a = -\log(1.4 \times 10^{-5}) = 4.85$$

### % ionization

$$\% \text{ ionization} = \frac{\text{moles ionized per liter}}{\text{moles available per liter}} \times 100\%$$

$$= \frac{x}{c} = \frac{0.00041}{0.012} \times 100\% = 3.4\%$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

466

---

---

---

---

---

---

---

### Your Turn!

**Ex.** The base ionization constant for methylamine is  $4.4 \times 10^{-4}$ . What is the pH of a 0.050 M solution of this base ?

- A. 1.03
- B. 2.33
- C. 11.67
- D. 12.97

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

467

---

---

---

---

---

---

---

### Your Turn! - Solution

$$K_b = 4.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{x^2}{0.05 - x}$$

Assume  $x$  is small

$$4.4 \times 10^{-4} = \frac{x^2}{0.05 - x} \quad x^2 = 2.2 \times 10^{-5}$$

$$x = 4.69 \times 10^{-3} \quad \text{pOH} = -\log(4.69 \times 10^{-3}) = 2.33$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.33 = 11.67$$

Jespersen/Brady/Hyslop

Chemistry: The Molecular Nature of Matter, 6E

468

---

---

---

---

---

---

---