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Chapter 11

Intermolecular Forces and Liquids and Solids

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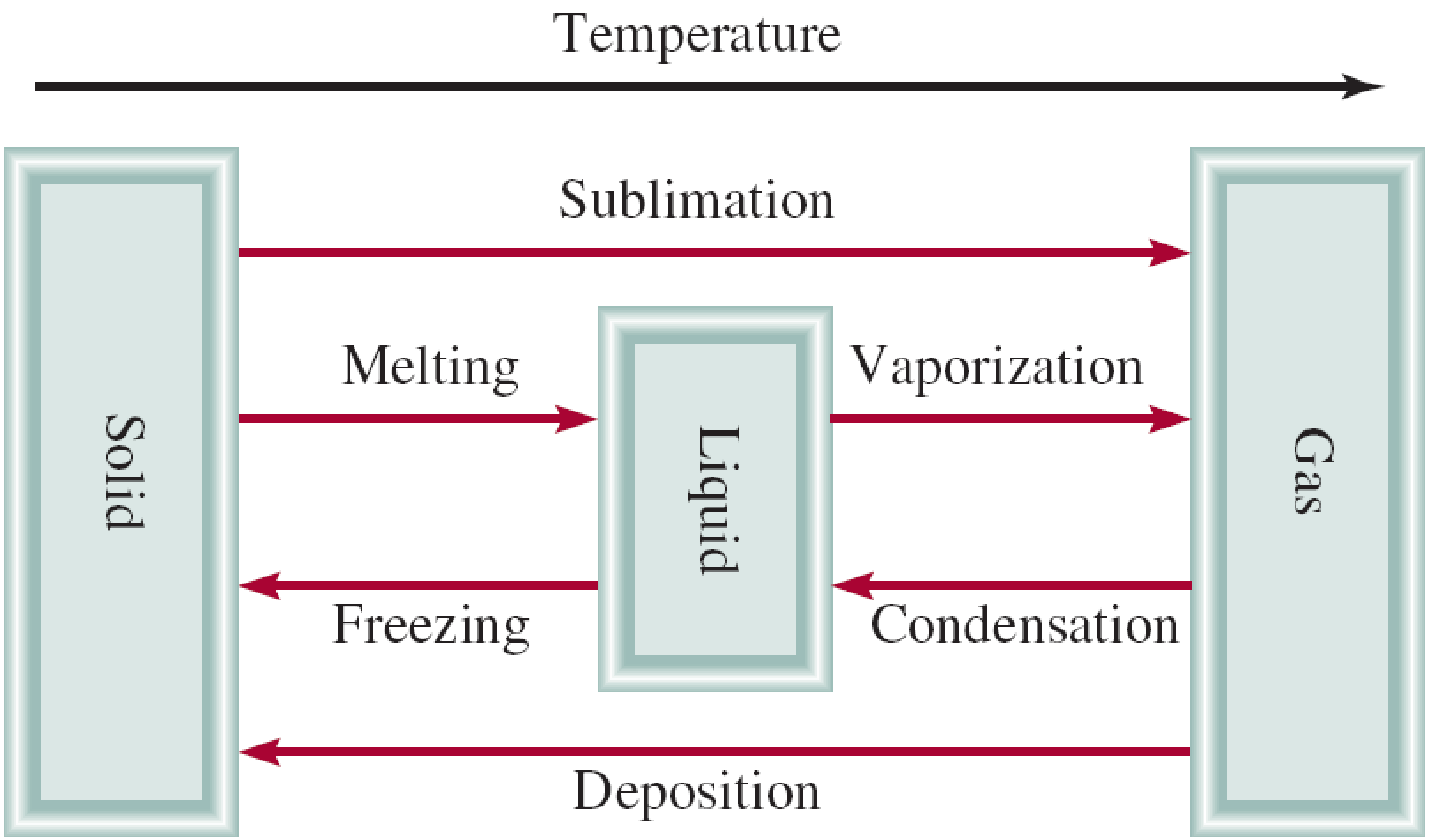
11.8
Phase Changes

Three phases of matter: gas, liquid, and solid.

Phase changes: transformations from one phase to another, occur when energy (usually in the form of heat) is added or removed from a substance.

Phase changes are physical changes characterized by changes in molecular order; molecules in the solid phase have the greatest order, and those in the gas phase have the greatest randomness.

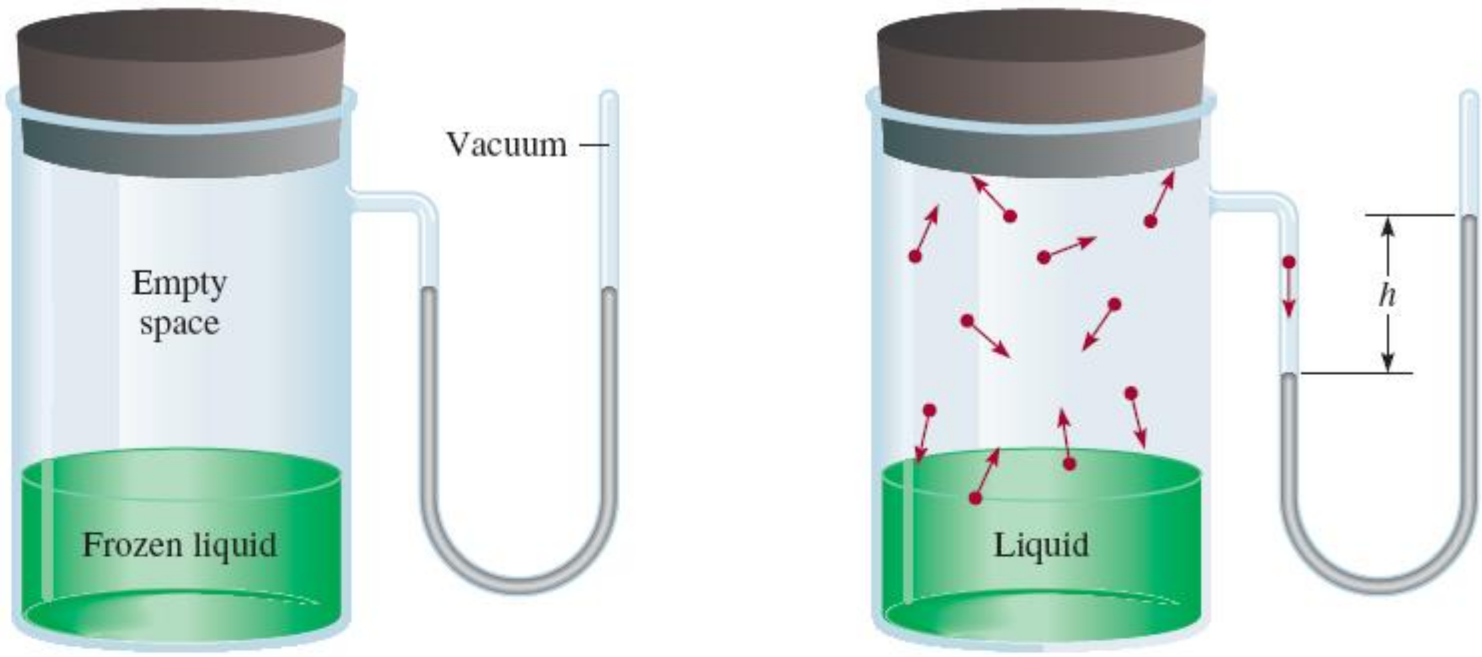


- **Liquid-Vapor Equilibrium**
- **Liquid-Solid Equilibrium**
- **Solid-Vapor Equilibrium**

Liquid-Vapor Equilibrium

Evaporation, or **vaporization,** is the process in which a liquid is transformed into a gas.

Vapor Pressure …



Apparatus for measuring the vapor pressure of a liquid. Initially the liquid is frozen so there are no molecules in the vapor phase. On heating, a liquid phase is formed and evaporization begins. At equilibrium, the number of molecules leaving the liquid is equal to the number of molecules returning to the liquid. The difference in the mercury levels (h) gives the equilibrium vapor pressure of the liquid at the specified temperature.

Condensation, the change from the gas phase to the liquid phase, occurs because a molecule strikes the liquid surface and becomes trapped by intermolecular forces in the liquid.

Molar Heat of Vaporization …

A measure of the strength of intermolecular forces in a liquid is the **molar heat of vaporization (**ΔH_{vap}**)**, defined as the energy (usually in kilojoules) required to vaporize 1 mole of a liquid.

The molar heat of vaporization is directly related to the strength of intermolecular forces that exist in the liquid.

The equilibrium vapor pressure (*P*) of a liquid should increase with increasing temperature. The quantitative relationship between the vapor pressure *P* of a liquid and the absolute temperature *T* is given by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H_{\mathrm{vap}}}{RT} + C$$

Where; *R* is the gas constant (8.314 J/K mol), and *C* is a constant.

By measuring the vapor pressure of a liquid at different temperatures

At temperatures T_1 and T_2, the vapor pressures are P_1 and P_2.

$$\ln P_1 = -\frac{\Delta H_{\text{vap}}}{RT_1} + C$$

$$\ln P_2 = -\frac{\Delta H_{\text{vap}}}{RT_2} + C$$

$$\longrightarrow$$

$$\begin{aligned}\ln P_1 - \ln P_2 &= -\frac{\Delta H_{\text{vap}}}{RT_1} - \left(-\frac{\Delta H_{\text{vap}}}{RT_2}\right) \\ &= \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned}$$

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

EXAMPLE

Diethyl ether is a volatile, highly flammable organic liquid that is used mainly as a solvent. The vapor pressure of diethyl ether is 401 mmHg at 18°C. Calculate its vapor pressure at 32°C (ΔH_{vap} = 26.0 kJ/mol).

$$P_1 = 401 \text{ mmHg} \qquad P_2 = ?$$
$$T_1 = 18°\text{C} = 291 \text{ K} \qquad T_2 = 32°\text{C} = 305 \text{ K}$$

$$\ln\frac{401}{P_2} = \frac{26{,}000 \text{ J/mol}}{8.314 \text{ J/K} \cdot \text{mol}}\left[\frac{291 \text{ K} - 305 \text{ K}}{(291 \text{ K})(305 \text{ K})}\right]$$
$$= -0.493$$

Taking the antilog of both sides

$$\frac{401}{P_2} = e^{-0.493} = 0.611$$

P_2 = 656 mmHg

Practice Exercise

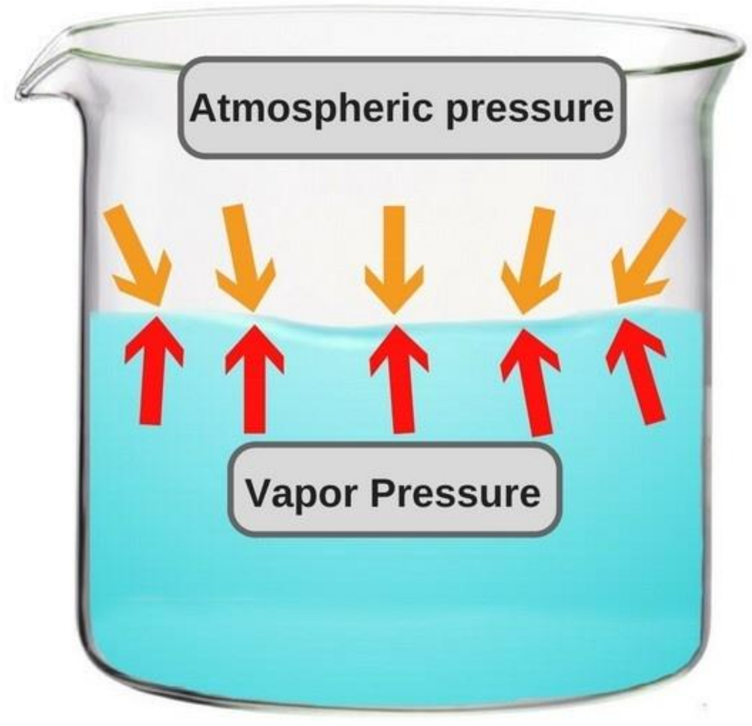
The vapor pressure of ethanol is 100 mmHg at 34.9°C. What is its vapor pressure at 63.5°C? (ΔH_{vap} for ethanol is 39.3 kJ/mol).

Boiling Point …

Every liquid has a temperature at which it begins to boil.

The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure.

The normal boiling point of a liquid is the temperature at which it boils when the external pressure is 1 atm.



Liquid-Solid Equilibrium

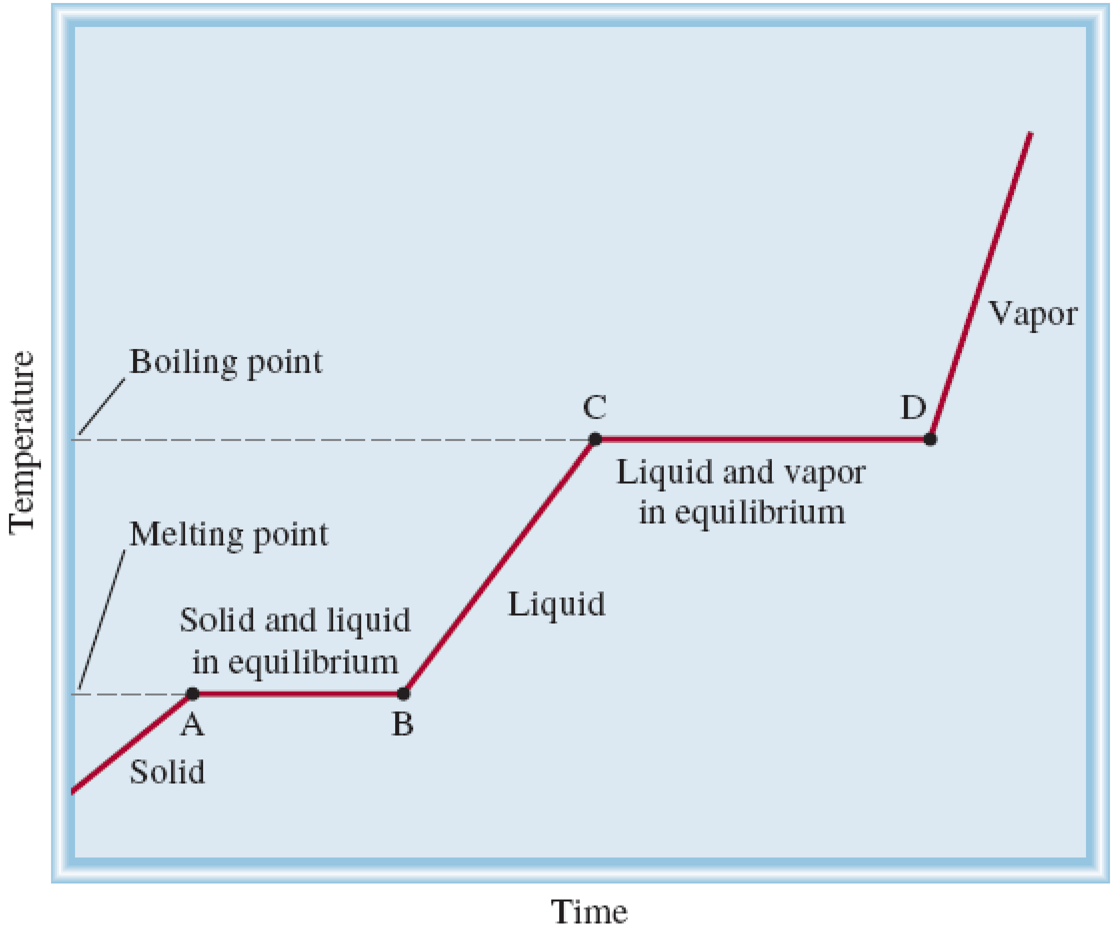
The transformation of liquid to solid is called freezing, and the reverse process is called melting, or fusion. The **melting point** of a solid or the **freezing point** of a liquid is the temperature at which solid and liquid phases coexist in equilibrium. The normal melting (or freezing) point of a substance is the temperature at which a substance melts (or freezes) at 1 atm pressure.

Molar heat of fusion …

Molar heat of fusion (ΔH_{fus}) is the energy required to melt 1 mole of a solid.

ΔH_{fus} is smaller than ΔH_{vap}. This is consistent with the fact that molecules in a liquid are still fairly closely packed together, so that some energy is needed to bring about the rearrangement from solid to liquid.

On the other hand, when a liquid evaporates, its molecules become completely separated from one another and considerably more energy is required to overcome the attractive force.



A typical heating curve, from the solid phase through the liquid phase to the gas phase of a substance. Because ΔH_{fus} is smaller than ΔH_{vap}, a substance melts in less time than it takes to boil. This explains why AB is shorter than CD. The steepness of the solid, liquid, and vapor heating lines is determined by the specific heat of the substance in each state.

Solid-Vapor Equilibrium

Sublimation is the process in which molecules go directly from the solid into the vapor phase.

Deposition is the reverse process, that is, molecules make the transition from vapor to solid directly.

Molar heat of sublimation …

Because molecules are more tightly held in a solid, the vapor pressure of a solid is generally much less than that of the corresponding liquid. **Molar heat of sublimation (ΔH_{sub})** of a substance is the energy required to sublime 1 mole of a solid. It is equal to the sum of the molar heats of fusion and vaporization:

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$


Thank You!