

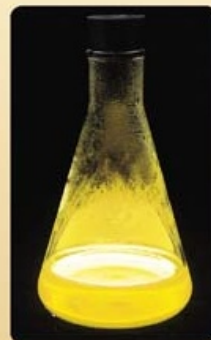
### Reduction of an ion containing vanadium(V) with zinc metal

The yellow color of the  $\text{VO}_2^+$  ion in acid solution.

Zn added. With time the yellow  $\text{VO}_2^+$  ion is reduced to blue  $\text{VO}^{2+}$  ion.

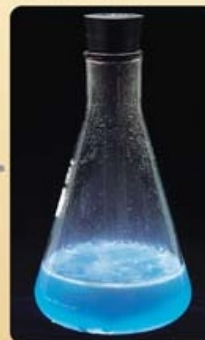
With time the blue  $\text{VO}^{2+}$  ion is further reduced to green  $\text{V}^{3+}$  ion.

Finally, green  $\text{V}^{3+}$  ion is reduced to violet  $\text{V}^{2+}$  ion.



$\text{VO}_2^+$

Add Zn →



$\text{VO}^{2+}$



$\text{V}^{3+}$



$\text{V}^{2+}$

© 2003 Thomson - Brooks/Cole

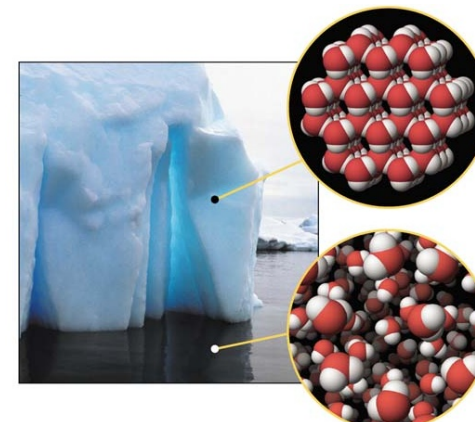
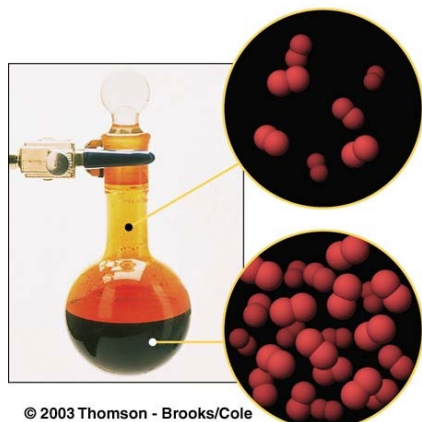
# CHEMISTRY 2000

## Topic #2: Thermochemistry and Electrochemistry – What Makes Reactions Go?

Fall 2020

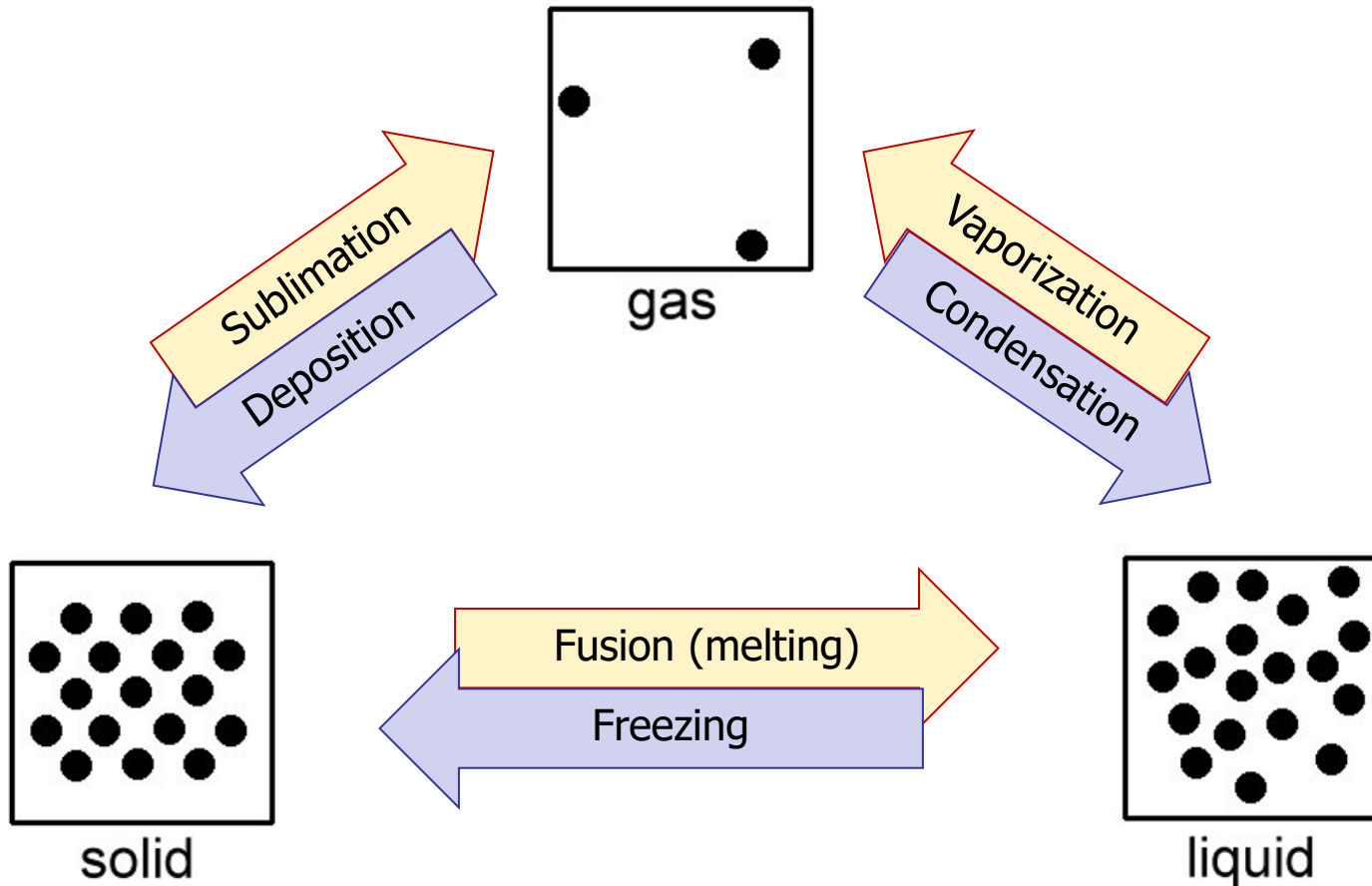
Dr. Susan Findlay

See Exercises 8.1 to 8.4



# Phase Changes

- Phase changes are equilibrium processes :





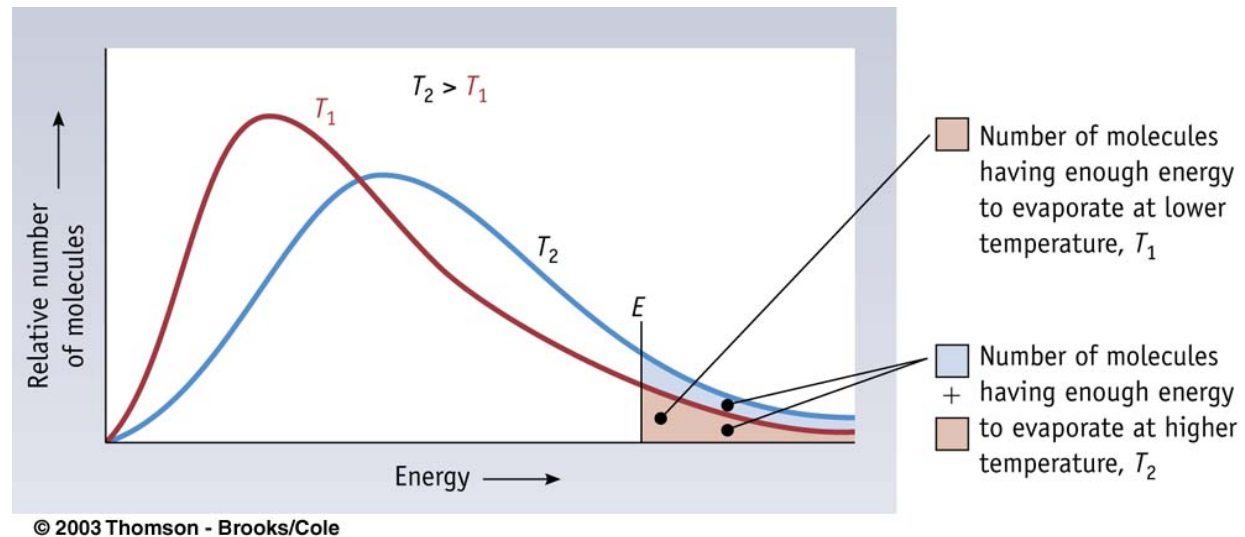
# Phase Changes

---

- Phase changes can be described using chemical equations:
  - Endothermic phase changes absorb heat:
    - Fusion (melting):
    - Vaporization (evaporation):
    - Sublimation:
  - Exothermic phase changes release heat:
    - Freezing:
    - Condensation:
    - Deposition:

# Vapour Pressure of Pure Substances

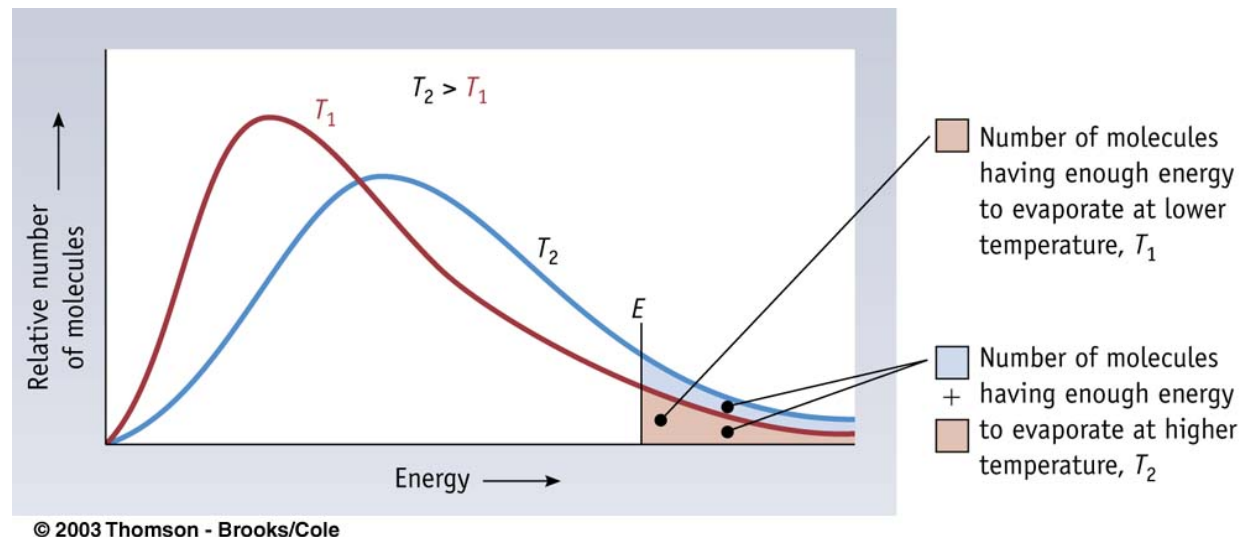
- When you leave wet dishes on a draining board overnight, they will usually be dry the next morning. The water has evaporated – even though your kitchen was 70-80°C below the boiling point of the water! How is this possible?



At any given temperature, some of the molecules in the liquid will have enough energy to escape the intermolecular forces holding the sample together.

# Vapour Pressure of Pure Substances

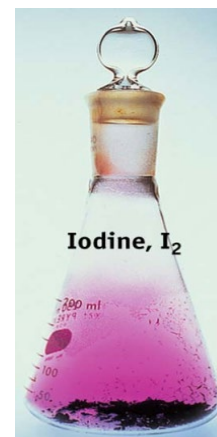
- Heating the liquid increases the rate of vaporization by increasing the proportion of molecules having enough energy to escape the intermolecular forces holding the liquid particles near each other.



- The surroundings can also supply heat slowly and steadily, which is why you don't notice your dishes getting cold as they dry.
- If you don't apply heat, rapid vaporization cools a liquid. Why?

# Vapour Pressure of Pure Substances

- Because there will always be at least a few molecules in a liquid with enough energy to evaporate, there will always be a layer of gas molecules immediately above a liquid. The pressure exerted by these gas molecules is referred to as the **vapour pressure**.
- The vapour pressure in a sealed container that has reached equilibrium is the **equilibrium vapour pressure** (though many people shorten that to “vapour pressure”):



- Vapour pressure is not exclusive to liquids; many solids have a measurable vapour pressure. e.g. dry ice (CO<sub>2(s)</sub>), I<sub>2(s)</sub>



# Vapour Pressure of Pure Substances

---

- **When the vapour pressure of a liquid is equal to the atmospheric pressure, the liquid boils.** The upward pressure exerted by gas particles is equal to the pressure of the atmosphere pushing down on the liquid's surface. As such, bubbles of gas can form within the liquid (not just at its surface), they rise, and we observe boiling:
- The boiling point of a liquid is therefore pressure-dependent. To allow comparisons, we define the temperature at which the vapour pressure of a liquid is equal to **1 atmosphere** (1 atm) as a liquid's **normal boiling point**.
- The term used to indicate that a substance has a high vapour pressure and low boiling point is **volatile**.



# Vapour Pressure of Pure Substances

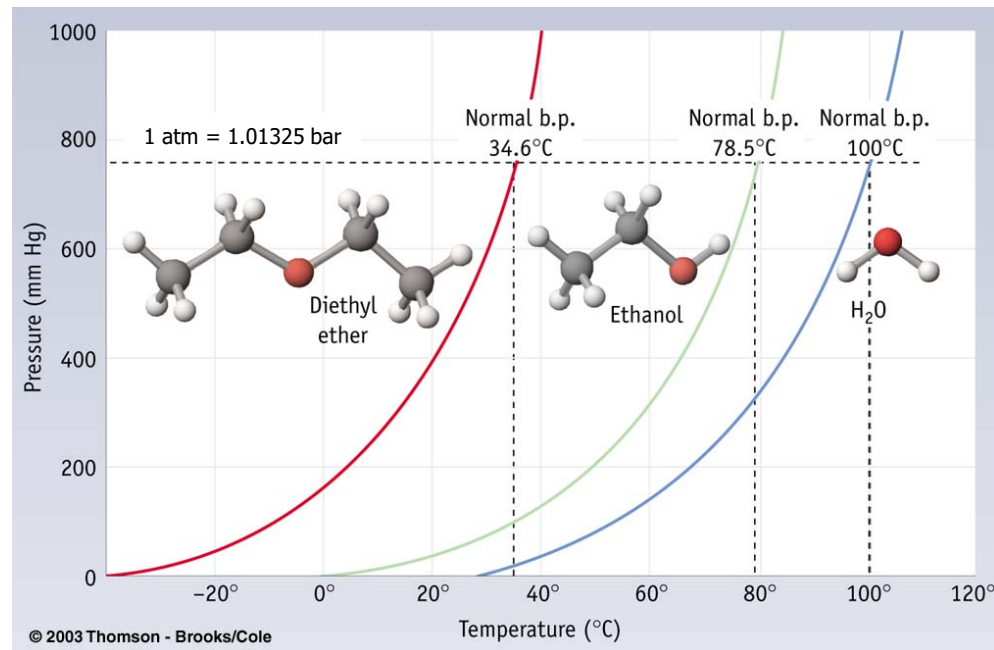
---

- Equilibrium vapour pressure can be read off a vapour pressure curve (*see next page*) or calculated from free energy data.
- The evaporation of water has  $\Delta_r G^\circ = +8.5 \frac{\text{kJ}}{\text{mol}}$ . What is the equilibrium vapour pressure for water at 25 °C ?



# Phase Diagrams

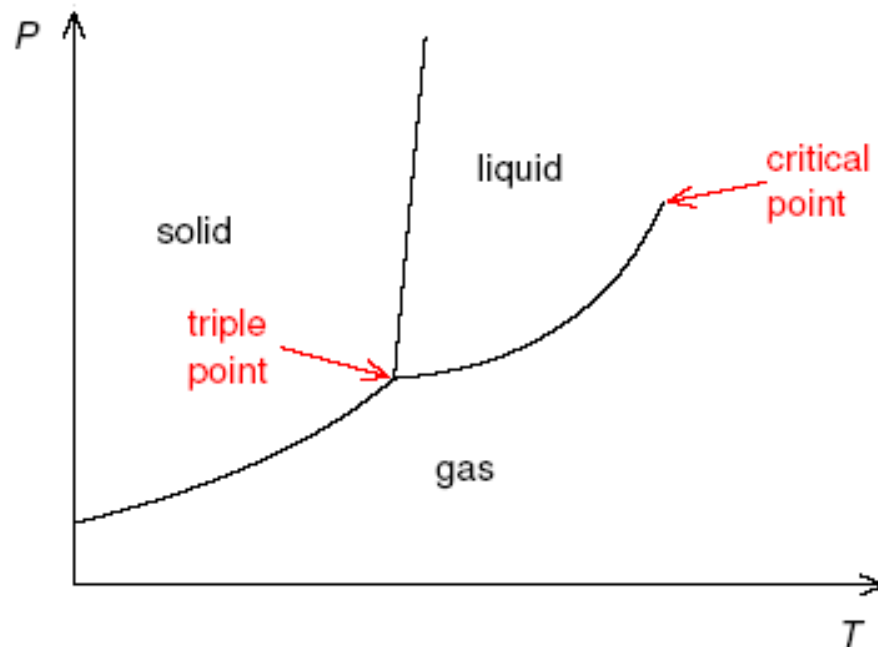
- Vapour pressure can be plotted against temperature, generating an exponential “vapour pressure curve”:



- This curve is part of a **phase diagram**, a figure which shows the most thermodynamically stable phases under different conditions. For pure substances, temperature-pressure phase diagrams are common.

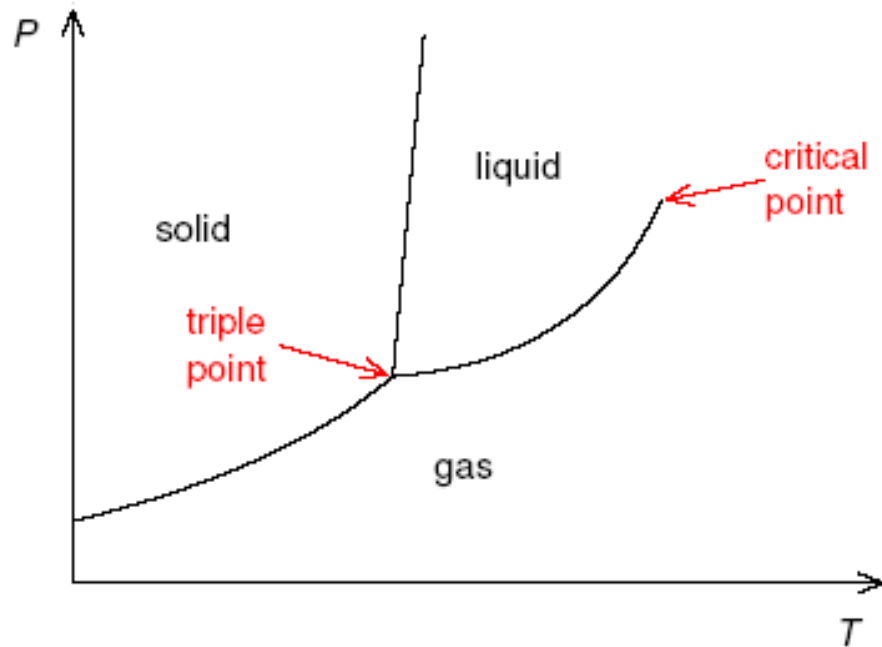
# Phase Diagrams

- A complete temperature-pressure phase diagram is shown below:



- Each line/curve on the diagram shows the conditions under which two phases are in equilibrium. The **triple point** shows the conditions under which all three phases are in equilibrium!
- At pressures and temperatures below the triple point, the liquid phase does not form. Solid sublimates directly to gas.

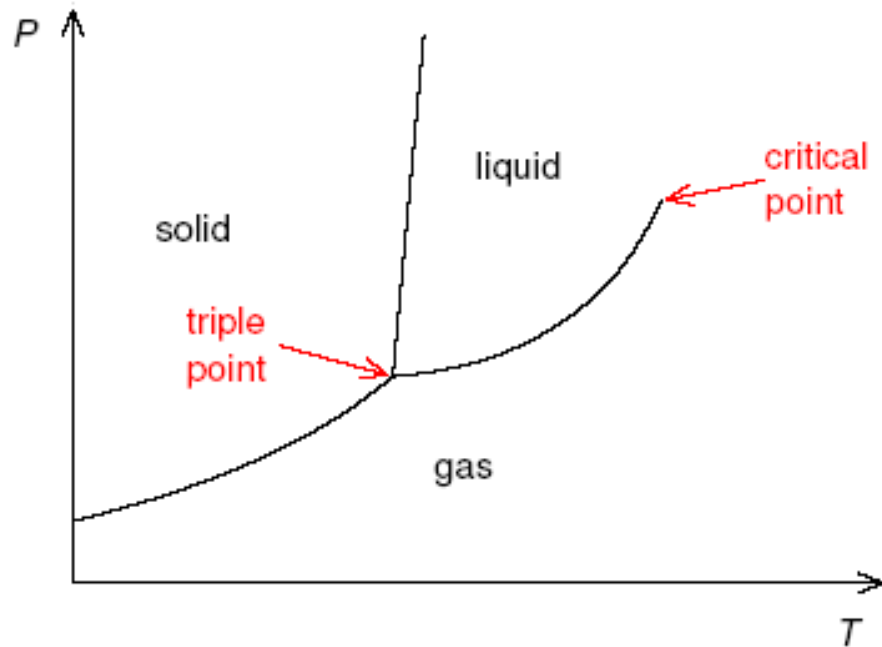
# Phase Diagrams



- A solid heated at a constant pressure will either:
  - undergo \_\_\_\_\_ to a liquid, or
  - undergo \_\_\_\_\_ to a gas.

Which occurs depends on the \_\_\_\_\_.

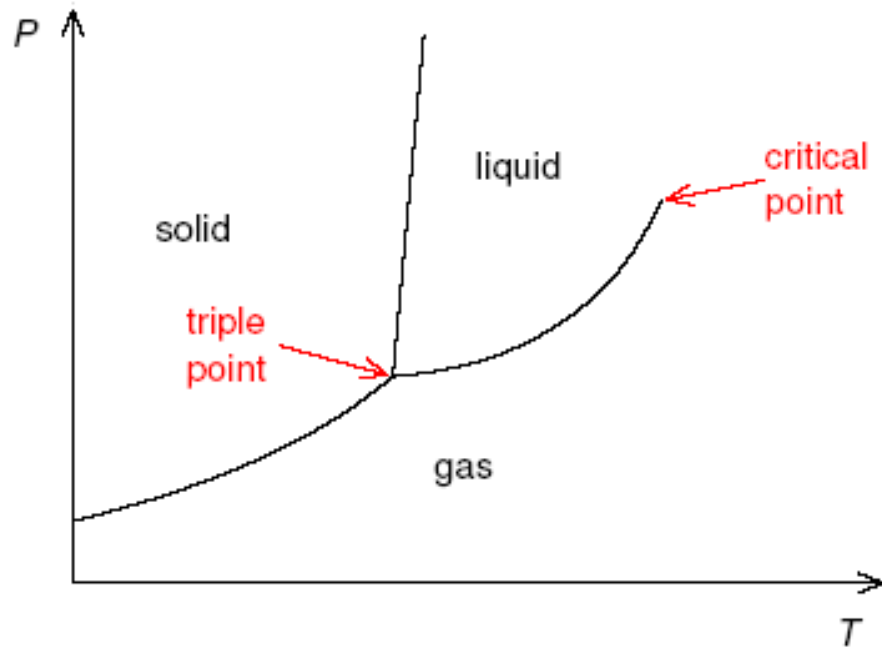
# Phase Diagrams



- A gas compressed at a constant temperature will either:
  - undergo \_\_\_\_\_ to a liquid, or
  - undergo \_\_\_\_\_ to a solid.

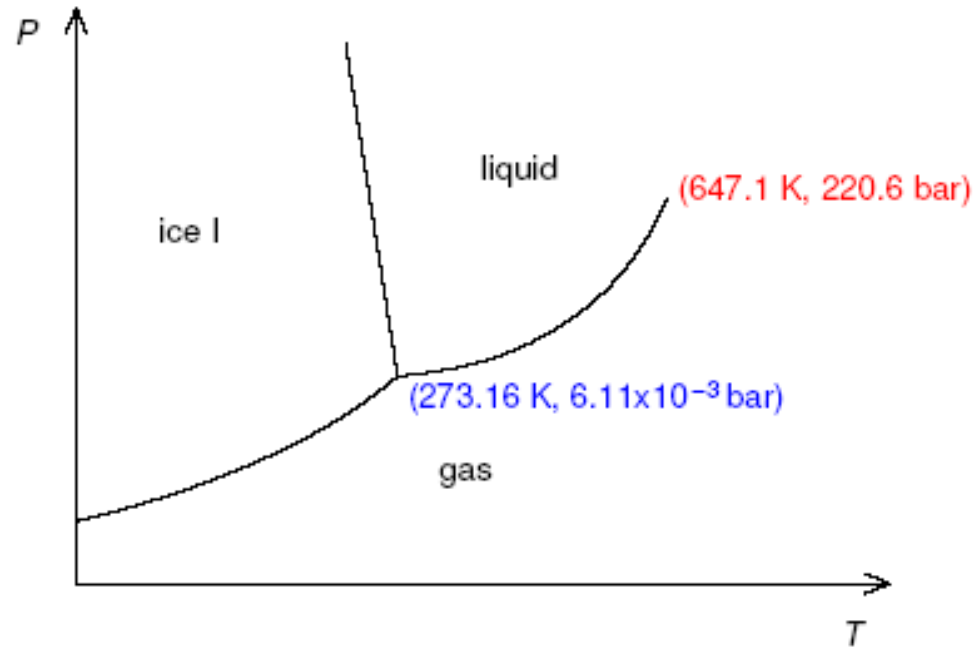
Which occurs depends on the \_\_\_\_\_.

# Phase Diagrams



- This diagram shows a typical phase diagram. The line between the solid and liquid phases has a positive slope. What does that indicate about the substance?

# Phase Diagrams



- This diagram shows a phase diagram for water. The line between the solid and liquid phases has a negative slope. What does that indicate about water?



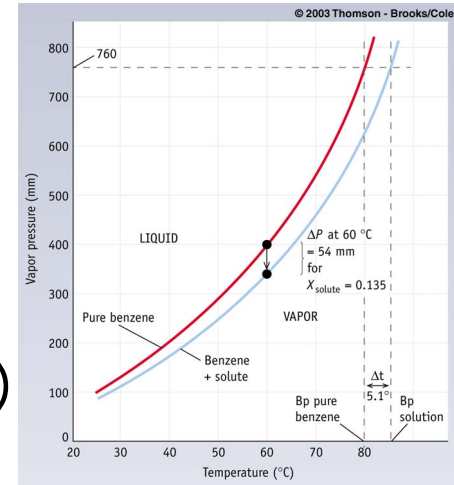
# Phase Diagrams

---

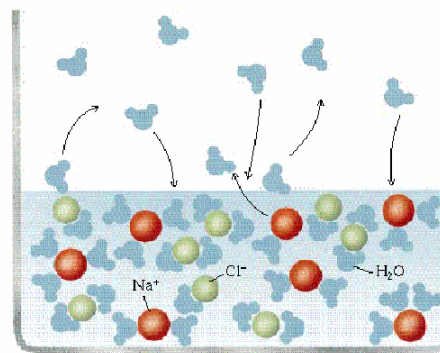
- Notice that, on both phase diagrams, the curve between the gas and liquid phase appears to stop. This is the **critical point**.
- As the temperature of a liquid increases, its vapour pressure increases, and it is necessary to have an increasingly high pressure in order to maintain the liquid state. There comes a temperature at which no amount of pressure is sufficient; the kinetic energy of the molecules is too great. This is the **critical temperature** (and the pressure is the **critical pressure**).
- At temperatures higher than the critical temperature, high pressures give a dense gas-like state called a **supercritical fluid**. The molecules in supercritical fluids are packed together almost as tightly as in liquids but they have enough energy to overcome intermolecular forces and move freely. As such, they can make excellent solvents (especially supercritical CO<sub>2</sub>).

# Vapour Pressure of Solutions

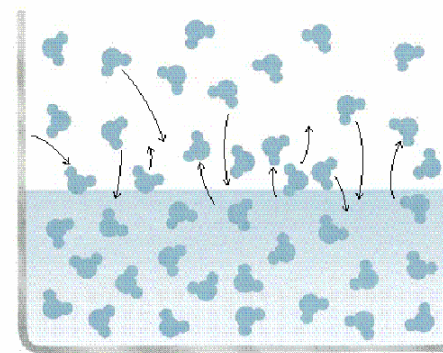
- The figure at the right shows vapour pressure curves for pure benzene (*in red*) and a 2 mol/kg solution (*in blue*) of a **nonvolatile solute** in benzene. Adding the solute has lowered the vapour pressure at any given temperature (thereby raising the boiling point) Why does this occur?



- Consider the difference between a pure liquid and a solution with a nonvolatile solute. *e.g. pure water (right) vs. salt water (left).*



(a) Sea water



(b) Pure water





# Vapour Pressure of Solutions

---

- The surface of pure water consists entirely of water molecules, a fraction of which have enough energy to evaporate.
- The surface of salt water consists primarily of water molecules but also some ions from the salt. The same fraction of water molecules has enough energy to evaporate but, since fewer water molecules are at the surface, fewer evaporate. Essentially, the salt ions are “blocking the surface” of the solution.
- Thus, salt water has a lower vapour pressure than the pure water. Because of this, salt water has to be heated to a higher temperature to raise its vapour pressure to be equal to atmospheric pressure.
- Thus, the boiling point of salt water is higher than that of pure water.



# Vapour Pressure of Solutions

---

- This can be expressed mathematically. **Raoult's law** defines the vapour pressure of a solvent ("A").

$$P_A = X_A P_A^\circ$$

where  $P_A$  is the vapour pressure of the solvent (in solution),  $P_A^\circ$  is the vapour pressure of the solvent (as a pure liquid) and  $X_A$  is the mole fraction of the solvent molecules.



# Vapour Pressure of Solutions

---

- Note that Raoult's law only calculates the vapour pressure of the solvent. If a solute is volatile, it will have a vapour pressure too!

$$[A] = k_H P_A$$

where  $[A]$  is the concentration of the volatile solute "A",  $P_A$  is the vapour pressure of the volatile solute and  $k_H$  is the Henry's law constant (solute-specific). Unsurprisingly, this is **Henry's law**. It is usually presented when discussing solubility of gases.



# Equilibrium Constant and Temperature

---

- An equilibrium constant ( $K$ ) is only constant as long as the temperature doesn't change! Why?
- The enthalpy and entropy change for a reaction vary slowly with temperature; however, the free energy change is strongly temperature-dependent:

$$\Delta G = \Delta H - T\Delta S$$

- At any temperature:

$$\Delta_r G^\circ(T) = -RT \ln[K(T)]$$

- So, as  $T$  changes,  $\Delta G$  changes and therefore  $K$  changes.



# Equilibrium Constant and Temperature

---

- When comparing a reaction at temperatures  $T_1$  and  $T_2$ , we can say that:

$$\Delta_r G_1^o(T_1) = \Delta_r H_1^o - T_1 \Delta_r S_1^o = -RT_1 \ln[K_1]$$

and

$$\Delta_r G_2^o(T_2) = \Delta_r H_2^o - T_2 \Delta_r S_2^o = -RT_2 \ln[K_2]$$



# Equilibrium Constant and Temperature

---

- If we approximate that the values of  $\Delta H$  and  $\Delta S$  don't change significantly over the given temperature range, we can combine these equations and simplify to get:

$$\ln K_2 - \ln K_1 = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

or:

$$\ln \left( \frac{K_2}{K_1} \right) = \frac{\Delta_r H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$



# Equilibrium Constant and Temperature

---

- You have probably been taught that  $K_w = 10^{-14}$  under standard conditions (making neutral water have  $pH$  7 at  $25^\circ C$ ).  
What is  $K_w$  at  $37.00^\circ C$ ?

$$\Delta_f H^\circ(OH_{(aq)}^-) = -230.0 \frac{kJ}{mol}$$
$$\Delta_f H^\circ(H_2O_{(l)}) = -285.8 \frac{kJ}{mol}$$



# Equilibrium Constant and Temperature

---





# Equilibrium Constant and Temperature

---

- What does this tell us about the  $pH$  of water at  $37.00^\circ C$ ?

$$pH = -\log(a_{H^+})$$



# Equilibrium Constant and Temperature

---

- Recall that the boiling point of a liquid is the temperature at which its vapour pressure equals the atmospheric pressure. If the atmospheric pressure in Lethbridge is typically 90 kPa, what is the boiling point of water on a typical day in Lethbridge?

$$\Delta_{\text{vap}} H_m^\circ(\text{H}_2\text{O}) = 40.66 \frac{\text{kJ}}{\text{mol}}$$



# Equilibrium Constant and Temperature

---



# Equilibrium Constant and Temp. (Solutions)

---

- The same approach can be used to calculate the boiling point (or freezing point) of aqueous solutions. When we salt roads, we make saturated salt solutions which freeze below  $0^{\circ}\text{C}$ . Calculate the freezing point of  $\text{NaCl}_{(aq)}$  prepared by dissolving 6 mol NaCl in 1 kg  $\text{H}_2\text{O}$ .

$$\Delta_{\text{fus}} H_m^{\circ}(\text{H}_2\text{O}) = 6.007 \frac{\text{kJ}}{\text{mol}}$$



# Equilibrium Constant and Temp. (Solutions)

---