

By the end of today's class you will be able to:

- 1) Describe the relative strength of intermolecular forces.
- 2) Describe phase transitions.
- 3) Calculate vapor pressure at varying temperatures using the Clausius-Clapeyron equation.

10/01/2014

PHASE TRANSITIONS and VAPOR PRESSURE

## Intermolecular Forces?

- Many gases behave as ideal gases at high temperature and low pressure **where intermolecular forces do not play a large role.**
- What are these intermolecular forces and where do they fit in?

## van der Waals forces

Weak forces between groups of atoms or molecules.

We will discuss two types:

- ① London Dispersion Force (instantaneous dipole-induced dipole interaction).
- ② Dipole-dipole interactions.

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

---

### London Dispersion Force


Copyright © 2007 Pearson Education, Inc.


---

---

---

---

---

---

---

### Polarizability

- The tendency of charge distribution to become non-uniform in an atom or molecule is defined as its **polarizability**.
- What factors influence a molecule's polarizability?

• molecule shape  
 • more molecule weight  
means more  
polarizability

---

---

---

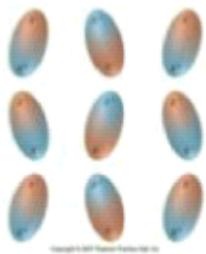
---

---

---

### Dipole-dipole Interactions

Polar molecules have a permanent dipole moment (a positive end and a negative end).




---

---

---

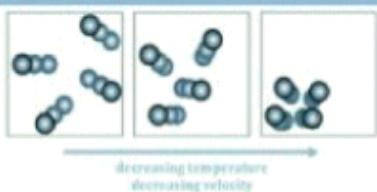
---

---

---

---

### So what does this have to do with gases?



- The temperature at which a liquid changes to a gas is its boiling point.
- Stronger intermolecular forces require a higher boiling point!

---

---

---

---

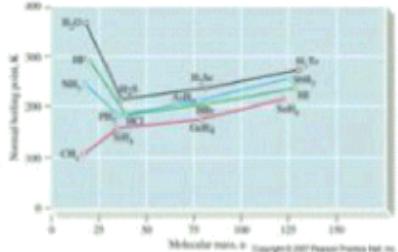
---

---

---

### Normal boiling points of some hydrides

Higher molecular mass  $\rightarrow$  higher polarizability  $\rightarrow$  stronger intermolecular force  $\rightarrow$  higher boiling point




---

---

---

---

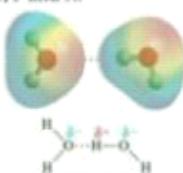
---

---

---

### Hydrogen Bonding [another intermolecular force]

- Highly electronegative atom pulls electrons away from H.
- H is attracted to lone pair of electrons on neighboring molecule.
- Occurs primarily between H and O, F and N.




---

---

---

---

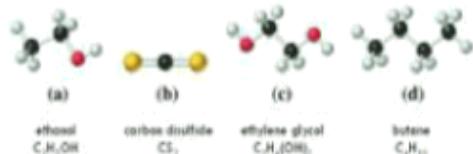
---

---

---

### Concept Check! (from Ch12)

4. Arrange the liquids represented by the following molecular models in the expected order of increasing normal boiling point.



(b), (d), (a), (c)

---



---



---



---



---

### Intermolecular Forces in Liquid

How does surface area affect overall intermolecular forces?



Higher surface area decreased overall intermolecular forces.

---



---



---



---



---

### Vaporization

- Phase change from liquid to gas.
- Occurs more readily at

- a)
- b)
- c)

---



---



---



---



---

## Enthalpy of Vaporization

- Enthalpy of vaporization is the amount of heat that must be absorbed to keep the liquid at constant temperature when a given quantity is vaporized.
- Higher intermolecular forces requires a higher enthalpy of vaporization!

$$\Delta H_{\text{vap}} = H_{\text{vapor}} - H_{\text{liquid}} = -\Delta H_{\text{condensation}}$$

Example:

- $\text{H}_2\text{O} (\text{l}) + 44.01 \text{ kJ/mol} \rightarrow \text{H}_2\text{O} (\text{g})$   
@ 25 °C and 1 atm:  $\Delta H_{\text{vap}} = 44.01 \text{ kJ/mol}$
- $\text{H}_2\text{O} (\text{g}) - 44.01 \text{ kJ/mol} \rightarrow \text{H}_2\text{O} (\text{l})$   
@ 25 °C and 1 atm:  $\Delta H_{\text{vap}} = -44.01 \text{ kJ/mol}$

## Enthalpy of Vaporization

TABLE 13.1 Some Enthalpies of Vaporization at 298 K\*

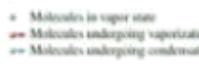
Liquid	$\Delta H_{\text{vap}}$ , kJ/mol
Diethyl ether, $(\text{C}_2\text{H}_5)_2\text{O}$	29.1
Methyl alcohol, $\text{CH}_3\text{OH}$	38.0
Ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$	42.6
Water, $\text{H}_2\text{O}$	44.0

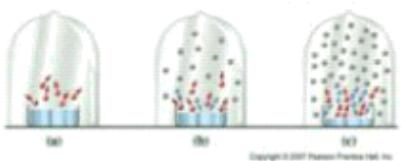
\*  $\Delta H_{\text{vap}}$  values are somewhat temperature-dependent (see Exercise 96).

Copyright © 2007 Pearson Prentice Hall, Inc.

## Phase Equilibrium

During phase equilibrium there is no net conversion of one phase to the other (both happen at equal rates).


 • Molecules in vapor state  
 ↗ Molecules undergoing vaporization  
 ↙ Molecules undergoing condensation



Copyright © 2007 Pearson Prentice Hall, Inc.

## Vapor Pressure

- Pressure measured when the system reaches equilibrium.
- Weak intermolecular forces →
- Strong intermolecular forces →
- $P_{\text{vap}} = f(T, \text{type of liquid})$

---

---

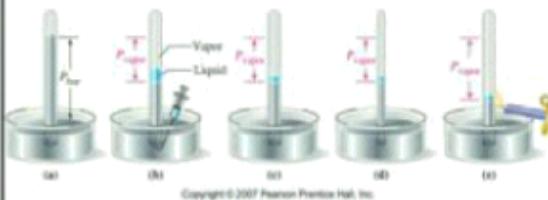
---

---

---

---

## Vapor Pressure




---

---

---

---

---

---

## Vapor Pressure of Water

TABLE 13.2 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg
0.0	4.6	20.0	30.0	40.0	588.6
10.0	9.2	30.0	51.8	94.0	610.9
20.0	17.5	40.0	55.3	95.0	633.9
21.0	18.7	50.0	92.5	96.0	657.6
22.0	19.8	60.0	149.4	97.0	682.1
23.0	21.1	70.0	233.7	98.0	707.3
24.0	22.4	80.0	359.3	99.0	733.2
25.0	23.8	90.0	525.8	100.0	760.0
26.0	25.2	91.0	546.0	110.0	1074.6
27.0	26.7	92.0	567.0	120.0	1489.1
28.0	28.3				

Vapor pressure is a function of temperature!!!

---

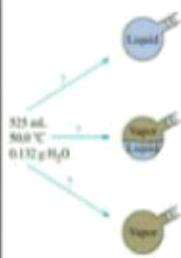
---

---

---

---

---

**Example 1:**

As a result of a chemical reaction, 0.132 g H<sub>2</sub>O is produced and maintained at a temperature of 50 °C in a closed flask. Will the water be present as a liquid only, vapor only or gas-liquid in equilibrium? The total volume of the product is 525 ml. Estimate the mass of liquid and the mass of vapor using the ideal gas law.

---

---

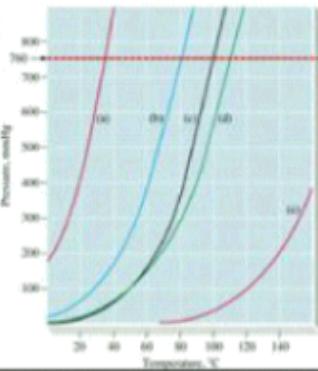
---

---

---

---

---

**Vapor Pressure Curves of Several Liquids****Normal Boiling Points**

- a) Diethyl ether, C<sub>2</sub>H<sub>5</sub>O
- b) Benzene, C<sub>6</sub>H<sub>6</sub>
- c) Water, H<sub>2</sub>O
- d) Toluene, C<sub>6</sub>H<sub>5</sub>
- e) Aniline, C<sub>6</sub>H<sub>5</sub>N

---

---

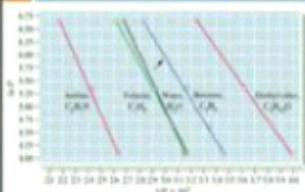
---

---

---

---

---

**Vapor Pressure Curves of Several Liquids**

$$y = mx + b$$

$$\ln P = -A\left(\frac{1}{T}\right) + B$$

$$A = \frac{\Delta H_{\text{vap}}}{R}$$

$$B = 0.3145 \text{ J/(mol·K)}$$

but what about B?

$$\ln P_2 - \ln P_1 = -A\left(\frac{1}{T_2}\right) + B - \left[-A\left(\frac{1}{T_1}\right) + B\right]$$

- Clapeyron-Claude Equation**
- Assumes  $\Delta H_{\text{vap}}$  does not vary with temperature.
  - Applies to other phase changes as long as the proper enthalpy is used.

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

---

---

---

---

---

---

---

## Antoine's Equation for $P_{\text{vap}}$

Another useful equation for vapor pressure:

$$\log P_{\text{vap}} = A - \frac{B}{C + T}$$

A, B and C are constants based on the type of substance under a given temperature range.

---



---



---



---



---



---

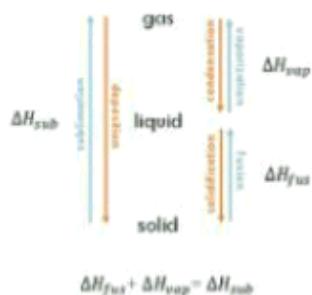


---



---

## Other Phase Changes




---



---



---



---



---



---



---



---

### Example 2:

#### Applying the Clausius-Clapeyron Equation

If liquid ammonia ( $\text{NH}_3$ ) has a normal boiling temperature of  $-33^\circ\text{C}$  and a vapor pressure of 100 mmHg at  $-68.5^\circ\text{C}$ , determine the value of  $\Delta H_{\text{vap}}$ .

Use this value to estimate the temperature at which liquid ammonia has a vapor pressure of 10 atm.

\*The actual temperature is  $25.7^\circ\text{C}$ .\*

---



---



---



---



---



---



---



---

**Example 3:**

In some areas, the winter snow sublimes into the air without melting.

- i) Use the heat of sublimation and the vapor pressure of ice at 0 °C to determine the pressure of the water vapor above ice at -20 °C.
- ii) Estimate the maximum concentration of water in the atmosphere using the ideal gas law.

Data:  $\Delta H_{\text{sub}} = 50.02 \frac{\text{kJ}}{\text{mol}}$  at 25 °C

$P_{\text{vap}}(0^\circ\text{C}) = 4.597 \text{ mmHg}$

$$R = 8.3145 \frac{\text{J}}{\text{molK}}$$

**Suggested Readings**

- 12.1 Intermolecular Forces
- 12.2 Some Properties of Liquids
- 12.3 Some Properties of Solids

$$\text{a) } \ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{P_2}{4.597 \text{ mmHg}}\right) = -\frac{50020 \frac{\text{J}}{\text{mol}}}{8.3145 \frac{\text{J}}{\text{molK}}} \left(\frac{1}{253.15 \text{ K}} - \frac{1}{\text{?}}\right)$$

$$\ln\left(\frac{P_2}{4.597 \text{ mmHg}}\right) = \# - \frac{1}{273.15 \text{ K}} \\ P_2 = 4.597 \text{ mmHg} \#$$

$$P_2 = 0.807 \text{ mmHg}$$

$$\text{b) } PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT} = C \leftarrow \text{concentration} \\ = \frac{0.807 \text{ atm}}{260 \text{ L}} =$$

$$(0.082058 \frac{\text{L atm}}{\text{molK}})(253.15 \text{ K})$$

$$= 5.11 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

Evaporation

- at the surface
- happens at T below boiling point
- At higher temp → vapor pressure is higher

Boiling

- throughout the liquid
- the T when vapor pressure is equal to surrounding atmospheric pressure