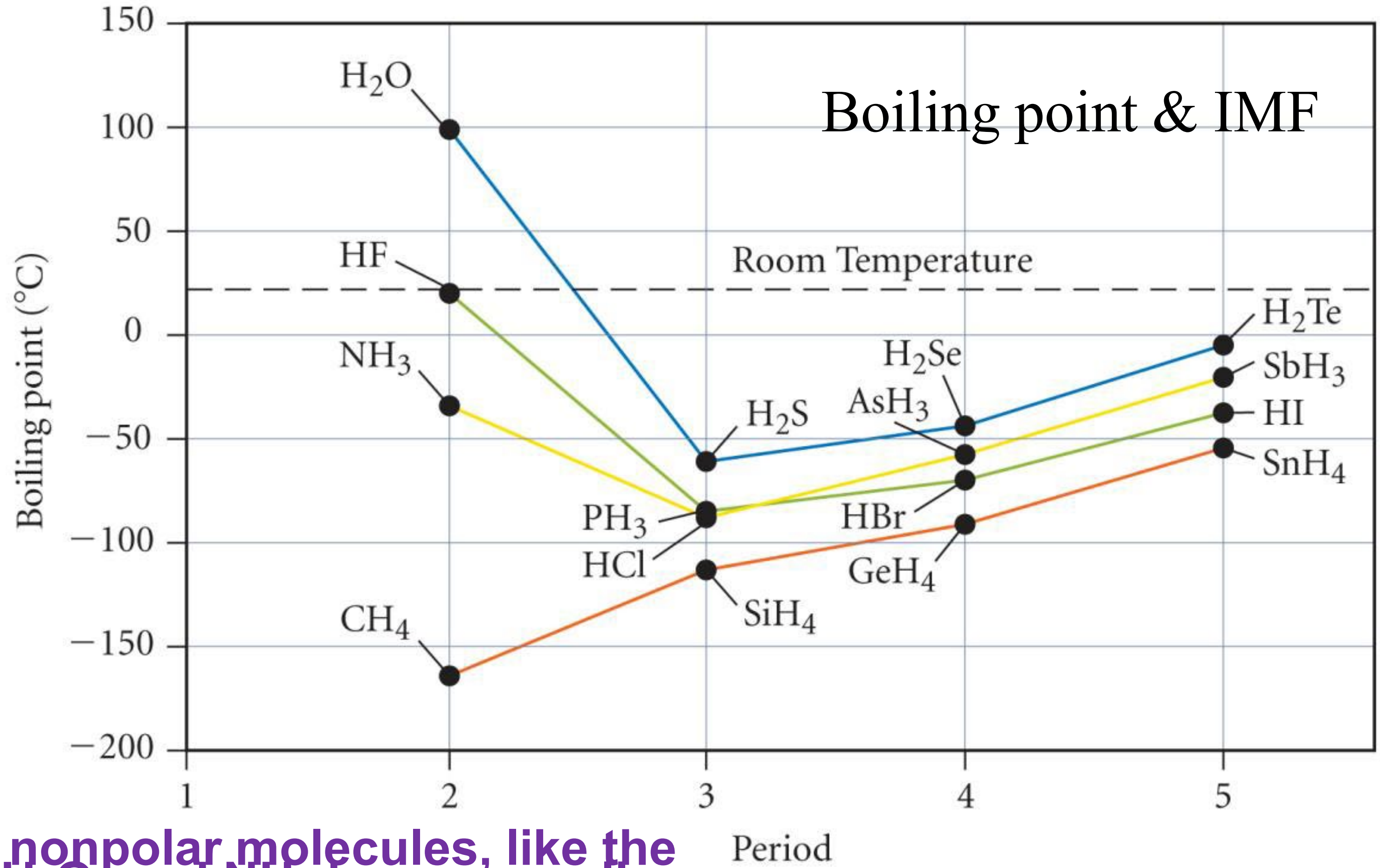
# LIQUIDS

Properties and
Effects

# Effect of Intermolecular Attraction on Evaporation and Condensation

- The weaker the attractive forces between molecules, the less energy they will need to vaporize.
- Also, weaker attractive forces means that more energy will need to be removed from the vapor molecules before they can condense.
- The net result will be more molecules in the vapor phase, and a liquid that evaporates faster—**the weaker the attractive forces, the faster the rate of evaporation**.
- Liquids that evaporate easily are said to be **volatile**.
  - *e.g., gasoline, fingernail polish remover*
  - *Liquids that do not evaporate easily are called **nonvolatile**.*
    - *e.g., motor oil*

# Boiling point & IMF




For nonpolar molecules, like the hydrides of group 4, the intermolecular attractions are due to dispersion forces. Therefore, they increase down the column causing the boiling point to increase.

$HF$, $H_2O$, and $NH_3$ have unusually strong dipole–dipole attractions called *hydrogen bonds*. Therefore, they have higher boiling points than you would expect from the general trends.

Polar molecules, like the hydrides of groups 5–7, have both dispersion forces and dipole–dipole attractions. Therefore, they have higher boiling points than the corresponding group 4 molecules.

# Attractive Forces and Solubility

- Solubility depends, in part, on the attractive forces of the solute and solvent molecules.
  - ***like dissolves like***
  - ***Miscible liquids will always dissolve in each other.***
- Polar substances dissolve in polar solvents.
  - ***hydrophilic groups = OH, CHO, C=O, COOH, $NH_2$, Cl***
- Nonpolar molecules dissolve in nonpolar solvents.
  - ***hydrophobic groups = C–H, C–C***
- Many molecules have both hydrophilic and hydrophobic parts. Solubility in water becomes a competition between the attraction of the polar groups for the water and the attraction of the nonpolar groups for their own kind.

# PROPERTIES OF LIQUIDS

## 1. VISCOSITY

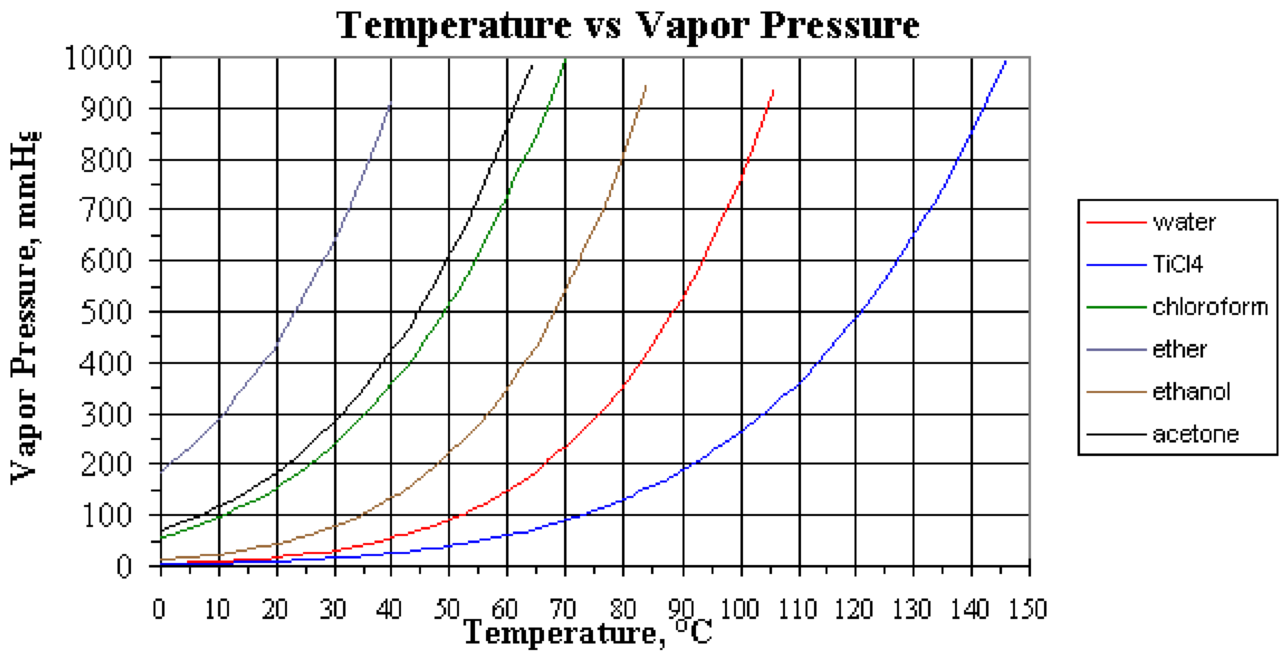
- The resistance of a liquid to flow
- Depends on attractive forces between molecules and structural features which cause greater interaction (entanglement).

## 2. SURFACE TENSION

- The energy required to increase the surface area of a liquid by a unit amount (E/A)
- Due to interactions between molecules and, *if* there are no molecules to interact with, the lack of interaction
- The layer of molecules on the surface behaves differently than the interior. The cohesive forces on the surface molecules have a net pull into the liquid interior.

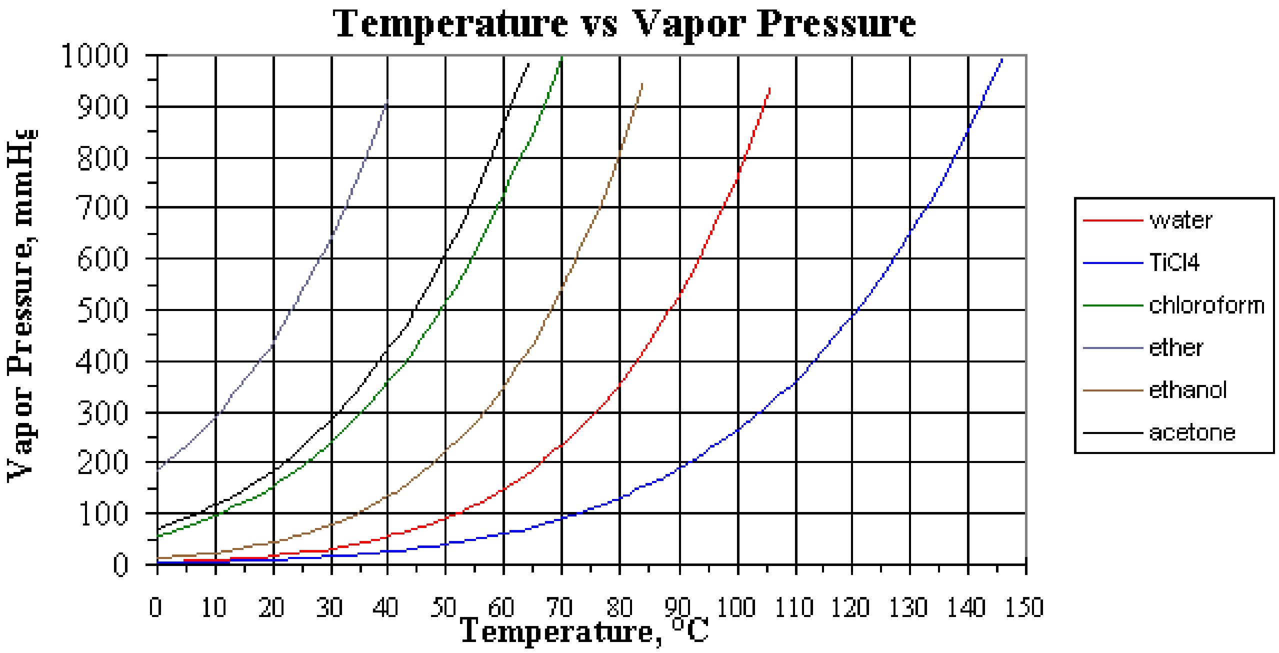
# Practice—Which of the following is the most volatile?

a) **water**
b) **$TiCl_4$**
c) **ether**
d) **ethanol**
e) **acetone**



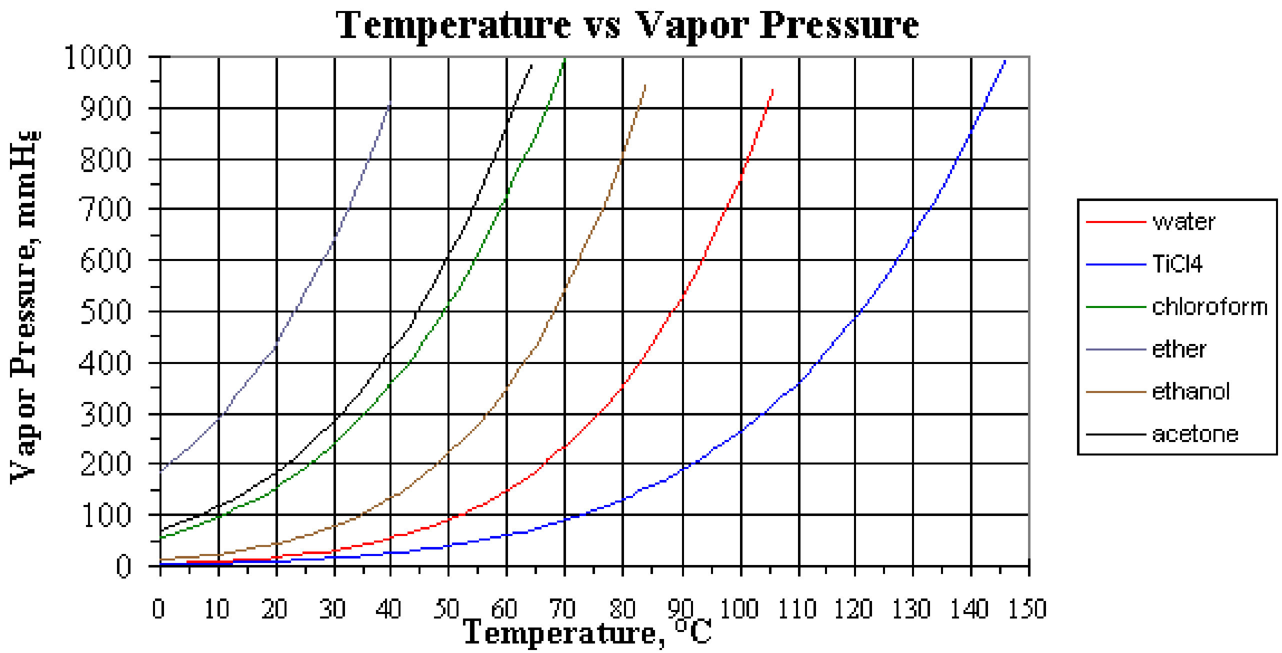
# Practice—Which of the following has the strongest intermolecular attractions?

a) **water**
b) **$TiCl_4$**
c) **ether**
d) **ethanol**
e) **acetone**



# Practice—Which of the following has the highest normal boiling point?

a) **water**
b) **$TiCl_4$**
c) **ether**
d) **ethanol**
e) **acetone**



# Lecture quiz 1

**As the temperature increases, do you expect the surface tension of a liquid to increase, decrease, or stay the same?**

a. Increase

b. Decrease

c. Stay the same

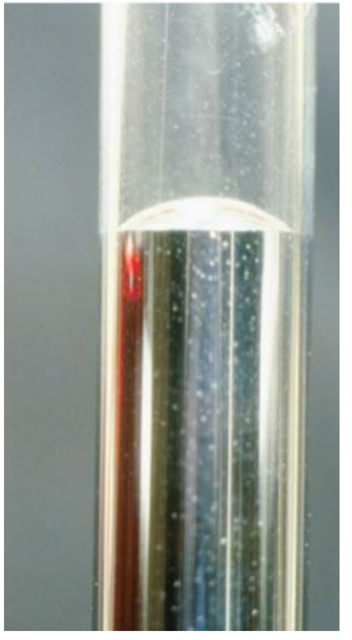
# Lecture quiz 2

**Which compound do you think is more volatile at 25 °C: $CCl_4$ or $CBr_4$?**

a. **$CBr_4$ because dispersion forces between its molecules are greater than in $CCl_4$**
b. **$CBr_4$ because polar forces between its molecules are smaller than in $CCl_4$**
c. **$CCl_4$ because polar forces between its molecules are greater than in $CBr_4$**
d. **$CCl_4$ because dispersion forces between its molecules are smaller than in $CBr_4$**

# Meniscus

- The curving of the liquid surface in a thin tube is due to the competition between adhesive and cohesive forces.
- The meniscus of water is concave in a glass tube because its adhesion to the glass is stronger than its cohesion for itself.
- The meniscus of mercury is convex in a glass tube because its cohesion for itself is stronger than its adhesion for the glass.
  – *Metallic bonds are stronger than intermolecular attractions.*



# VAPOR PRESSURE

**The pressure exerted by a vapor in equilibrium with its liquid or solid state.**

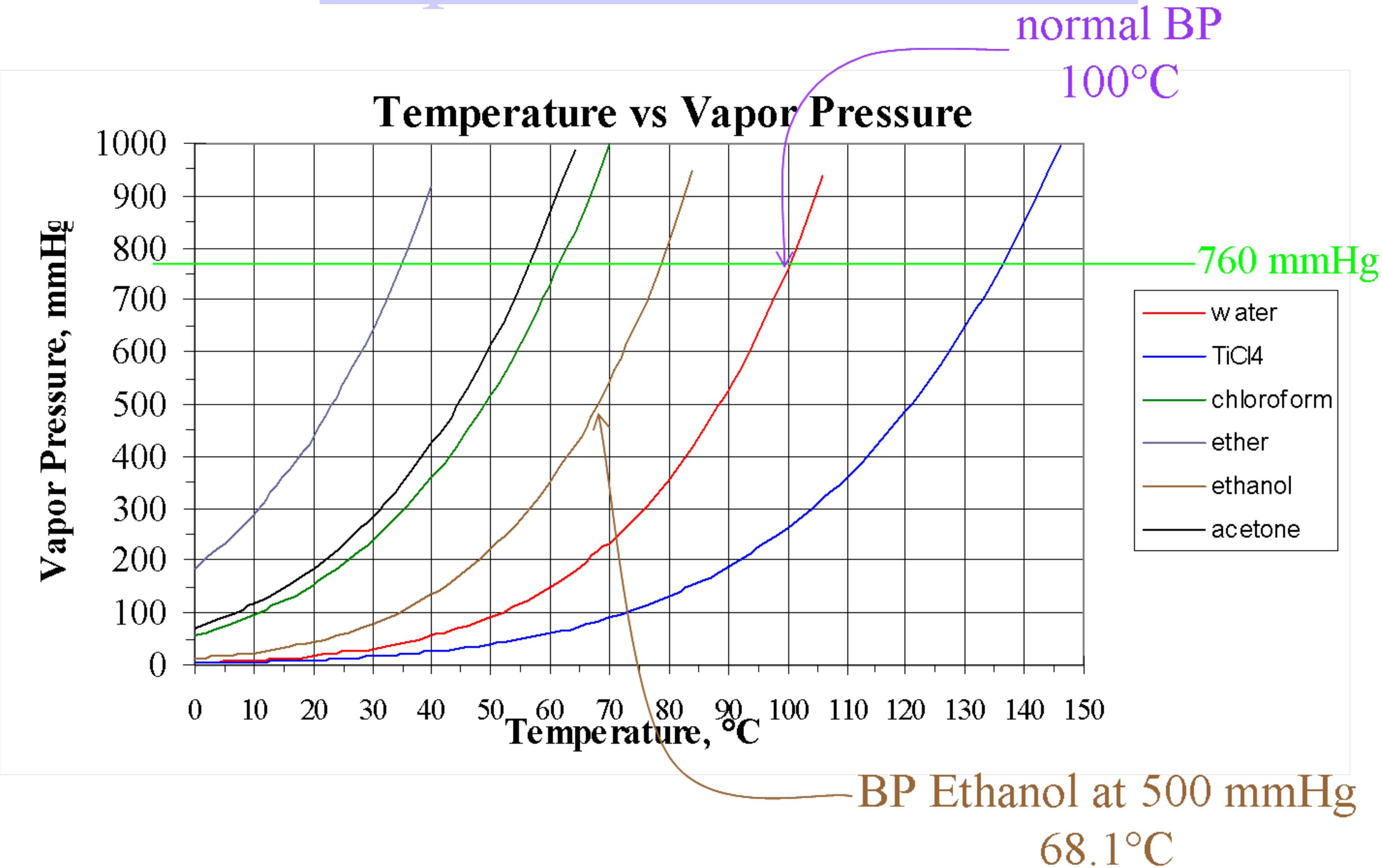
1. Vapor pressure changes with intermolecular forces and temperature

2. Vapor pressure involves a dynamic equilibrium liquid$\longleftrightarrow$gas

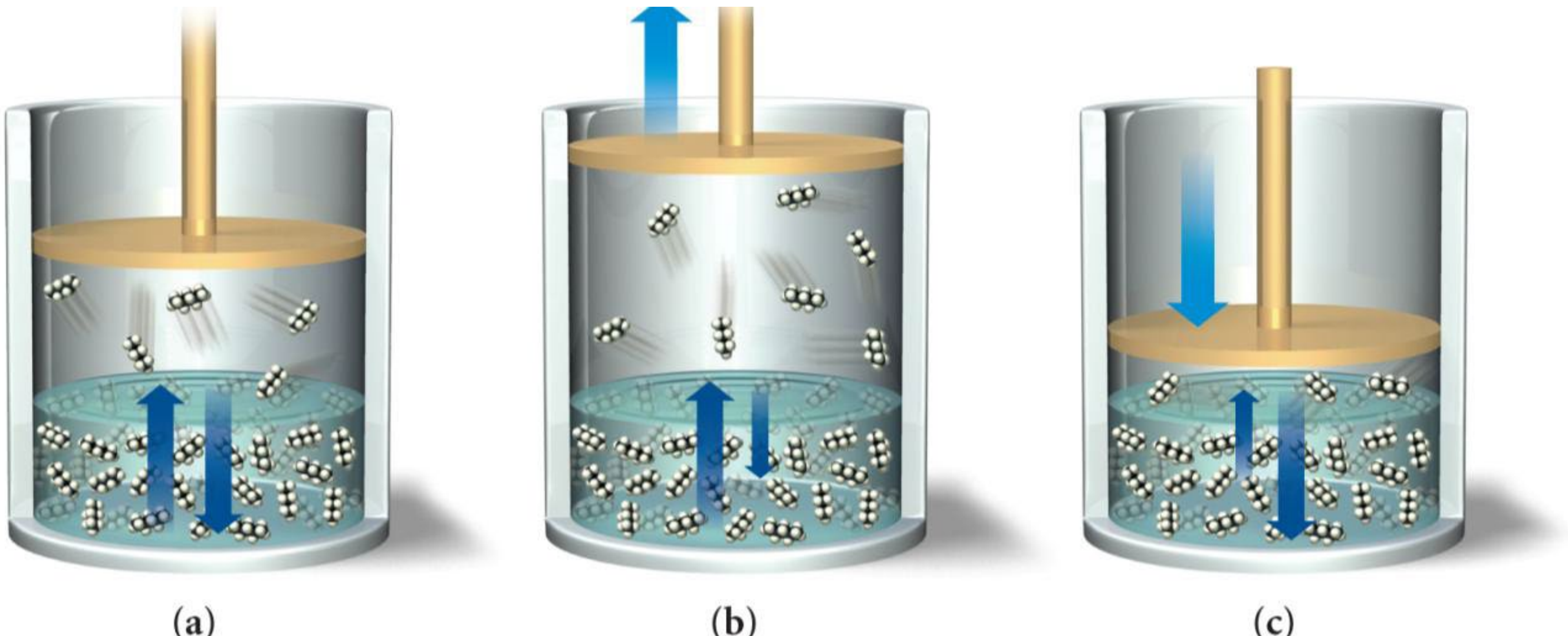
3. **Volatile vs nonvolatile**

4. Clausius - Clapeyron equation
-relates vapor pressure and liquid temperature

# 1. Vapor Pressure Curves



# 2. Changing the Container's Volume Disturbs the Equilibrium




**Initially, the rate of vaporization and condensation are equal and the system is in dynamic equilibrium.**

**When the volume is increased, the rate of vaporization becomes faster than the rate of condensation.**

**When the volume is decreased, the rate of vaporization becomes slower than the rate of condensation.**

# 4. CLAUSIUS - CLAPEYRON EQUATION

**In general, the higher the temperature, the weaker the intermolecular forces, and therefore the higher the vapor pressure. The non-linear relationship between vapor pressure and temperature is given by the Clausius - Clapeyron equation.**

**In P = $(-\Delta H_{vap}/RT) + C$ : a straight line if lnP vs. 1/T**

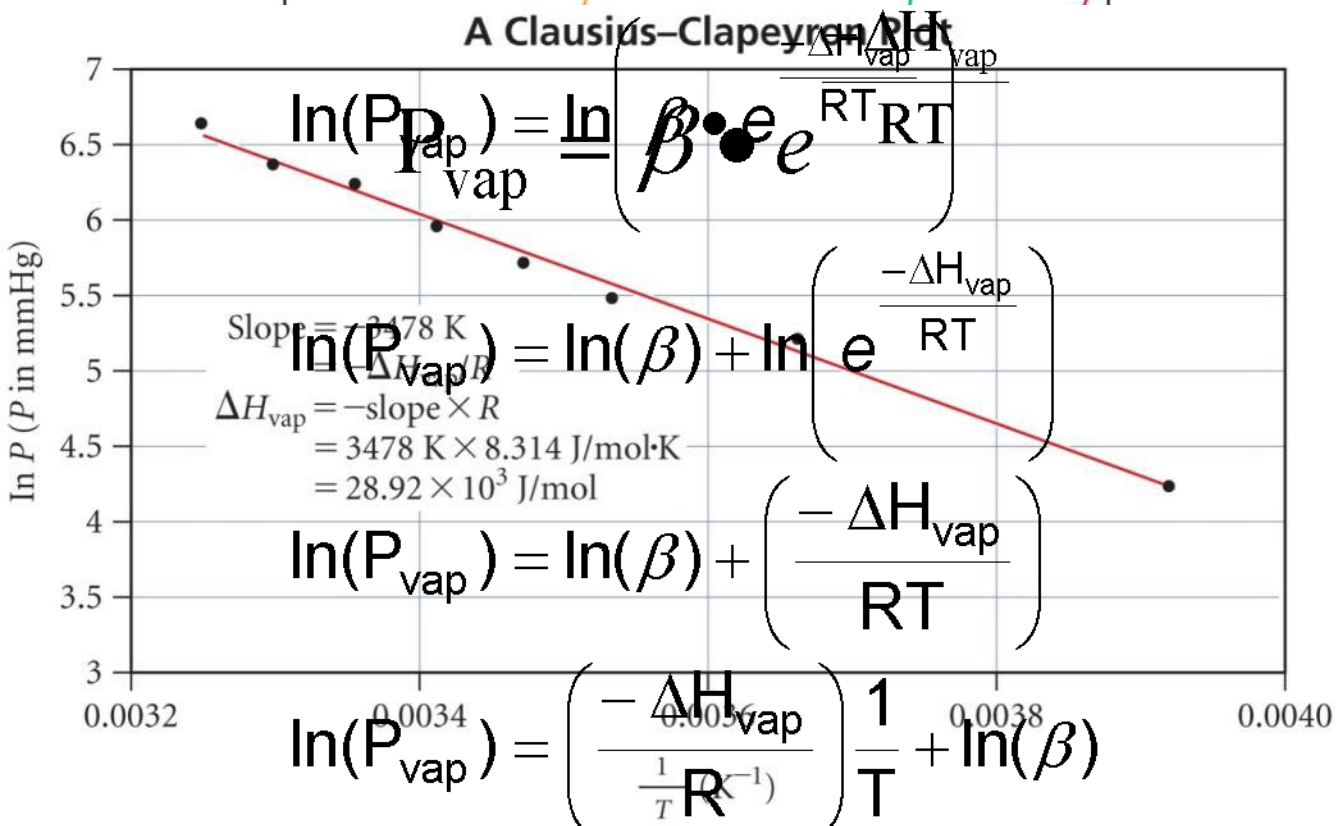
**It describes the amount of energy required to vaporize 1 mole of molecules in the liquid state**

**R = 8.31 J/mol K T = Kelvin P = vapor pressure**

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

# Clausius–Clapeyron Equation

- **A graph of $\ln(P_{vap})$ vs. 1/T is a straight line.**
- **The slope of the line × 8.314 J/mol∙K = $-\Delta H_{vap}$ in J/mol**
- **The logarithm of the vapor pressure vs. inverse absolute temperature is a linear fu**
- The graph of vapor pressure vs. temperature is an exponential growth curve.




$$P_{vap} = \beta e^{\frac{-\Delta H_{vap}}{RT}}$$

$$\ln(P_{vap}) = \ln\left(\beta \bullet e^{\frac{-\Delta H_{vap}}{RT}}\right)$$

$$\ln(P_{vap}) = \ln(\beta) + \ln\left(e^{\frac{-\Delta H_{vap}}{RT}}\right)$$

$$\ln(P_{vap}) = \ln(\beta) + \left(\frac{-\Delta H_{vap}}{RT}\right)$$

$$\ln(P_{vap}) = \left(\frac{-\Delta H_{vap}}{R}\right)\frac{1}{T} + \ln(\beta)$$

# Clausius–Clapeyron Equation Two-Point Form

- The equation below can be used with just two measurements of vapor pressure and temperature.
  - *However, it generally gives less precise results.*
    - *Fewer data points will not give as precise an average because there is less averaging out of the errors.*
      - *as with any other sets of measurements*
- can also be used to predict the vapor pressure if you know the heat of vaporization and the normal boiling point
  - *Remember: the vapor pressure at the normal boiling point is 760 torr.*

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

# Example : Calculate the vapor pressure of methanol at 12.0 °C.

| | |
|---|---|
| **Given:** | **$T_1$ = BP = 64.6 °C, $P_1$ = 760 torr, $\Delta H_{vap}$ = 35.2 kJ/mol, $T_2$ = 12.0 °C** |
| **Find:** | **$P_2$, torr** |
| **Conceptual Plan:** | $P_1, T_1, \Delta H_{vap}$ → $P_2$ |
| **Relationships:** | $T(K) = T(°C) + 273.15$    $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ |
| **Solution:** | |
| **Check:** | |

# Example : Calculate the vapor pressure of methanol at 12.0 °C. (2)

| | |
|---|---|
| **Given:** | **$T_1$ = BP = 337.8 K, $P_1$ = 760 torr, $\Delta H_{vap}$ = 35.2 kJ/mol, $T_2$ = 285.2 K** |
| **Find:** | **$P_2$, torr** |
| **Conceptual Plan:** | $P_1, T_1, \Delta H_{vap} \rightarrow P_2$ |
| **Relationships:** | $T(K) = T(°C) + 273.15$ <br> $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ |
| **Solution:** | $T_1 = 64.6 + 273.15 = 337.8\text{ K}$ <br> $T_2 = 12.0 + 273.15 = 285.2\text{ K}$ |
| **Check:** | |

# Example : Calculate the vapor pressure of methanol at 12.0 °C. (3)

| | |
|---|---|
| **Given:** | $T_1$ = BP = 337.8 K, $P_1$ = 760 torr, $\Delta H_{vap}$ = 35.2 kJ/mol, $T_2$ = 285.2 K |
| **Find:** | $P_2$, torr |
| **Conceptual Plan:** | $P_1, T_1, \Delta H_{vap} \rightarrow P_2$ |
| **Relationships:** | T(K) = T(°C) + 273.15 <br> $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ |
| **Solution:** | $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ <br> $\ln\left(\frac{P_2}{P_1}\right) = \frac{-35.2 \times 10^{3}\ \frac{J}{mol}}{8.314\ \frac{J}{mol\cdot K}}\left(\frac{1}{285.2\ K} - \frac{1}{337.8\ K}\right)$ |
| **Check:** | |

# Example : Calculate the vapor pressure of methanol at 12.0 °C. (4)

| | |
|---|---|
| **Given:** | **$T_1$ = BP = 337.8 K, $P_1$ = 760 torr, $\Delta H_{vap}$ = 35.2 kJ/mol, $T_2$ = 285.2 K** |
| **Find:** | **$P_2$, torr** |
| **Conceptual Plan:** | $P_1, T_1, \Delta H_{vap} \rightarrow P_2$ |
| **Relationships:** | **T(K) = T(°C) + 273.15** $\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ |

**Solution:**

$$\ln\left(\frac{P_2}{P_1}\right) = -2.31$$

$$\frac{P_2}{760\text{ torr}} = e^{-2.31} = 0.0993$$

$$P_2 = 75.4\text{ torr}$$

**Check:** **The units are correct, and the size makes sense since the vapor pressure is lower at lower temperatures.**

# Calculate the vapor pressure of water at 25.0 °C.

| | |
|---|---|
| **Given:** | $T_1$ = BP = 100.0 °C, $P_1$ = 760 torr, $\Delta H_{vap}$ = 40.7 kJ/mol, $T_2$ = 25.0 °C<br>$T_1$ = 373.2 K, $P_1$ = 760 torr, $\Delta H_{vap}$ = 40.7 kJ/mol, $T_2$ = 298.2 K |
| **Find:** | $P_2$, torr<br>$P_2$, torr |
| **Conceptual Plan:** | $P_1, T_1, \Delta H_{vap}$ → $P_2$<br>$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ |
| **Relationships:** | T(K) = T(°C) + 273.15 |
| **Solution:** | $T_1 = 100.0 + 273.15 = 373.2\ \text{K}$<br>$T_2 = 25.0 + 273.15 = 298.2\ \text{K}$<br>$\ln\left(\frac{P_2}{P_1}\right) = \frac{-40.7\times 10^3\ \frac{\text{J}}{\text{mol}}}{8.314\ \frac{\text{J}}{\text{mol}\bullet\text{K}}}\left(\frac{1}{298.2\ \text{K}} - \frac{1}{373.2\ \text{K}}\right)$<br>$\ln\left(\frac{P_2}{P_1}\right) = -3.30$<br>$\frac{P_2}{P_1} = e^{-3.30} = 0.0369$<br>$\frac{P_2}{760\ \text{torr}} = 0.0369$<br>$P_2 = 28.0\ \text{torr}$ |
| **Check:** | The units are correct, and the size makes sense since the vapor pressure is lower at lower temperatures. |

# LECTURE QUIZ #3

**1. List the intermolecular force(s) that pertain to the following compounds.**

**A) $C_6H_6$ B) $NH_2CH_2NH_2$ C) $CH_3CH_2NH_2$ D) HCN E) $CH_4$**

**2. Predict the relative surface tension, vapor pressure, volatility, and boiling point of the following substances by placing them in order of most to least.**

**A) $C_6H_6$ B) $NH_2CH_2NH_2$ C) $CH_3CH_2NH_2$ D) HCN E) $CH_4$**

**surface tension:**

**most: ________ ________ ________ ________ ________ least**

**vapor pressure:**

**most: ________ ________ ________ ________ ________ least**

**volatility:**

**most: ________ ________ ________ ________ ________ least**

**boiling point:**

**high: ________ ________ ________ ________ ________ LOW**