

Which has a lower Enthalpy?

- A. liquid iron
- B. solid iron ←
- C. they are exactly the same
- D. it depends on the temperature

Which has a higher Entropy?

- A. liquid iron ←
- B. solid iron
- C. they are exactly the same
- D. it depends on the temperature

Which has a lower Gibb's Free Energy?

- A. liquid iron
- B. solid iron
- C. they are exactly the same
- D. it depends on the temperature ←

### Equilibria

Balance between stability of  
lower Enthalpy (energy)  
& higher Entropy

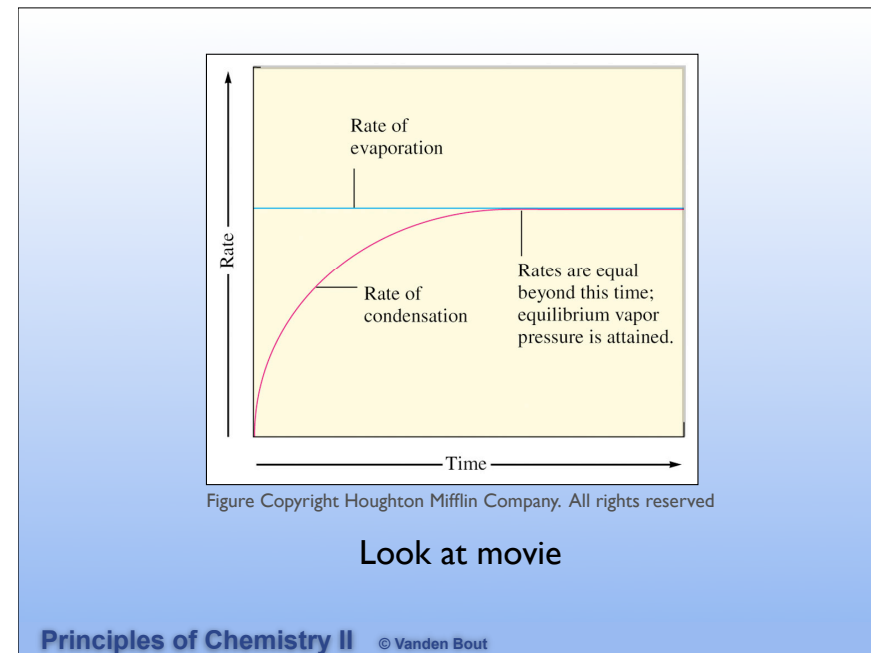
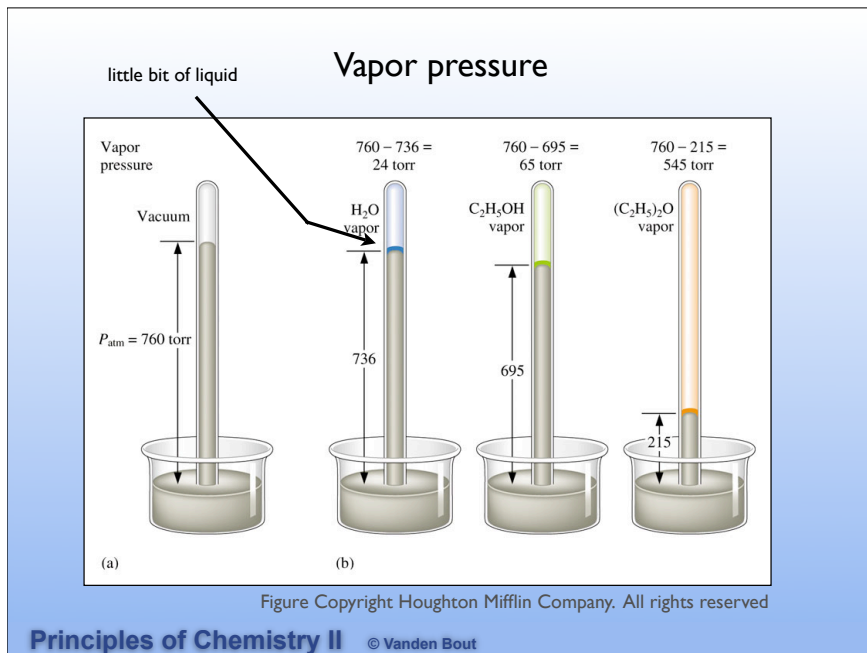
#### Physical Equilibria

Phase transitions (no "chemistry")

State with the lowest free energy is most stable

$$G = H - TS$$

therefore at high temperature  
the state with highest S will be the most stable



Look at movie

### Comparing different liquids

what matters is the free energy of the vapor compared to the liquid

For almost all substances the difference in **ENTROPY** between the vapor and the liquid is the same!

$$\Delta S_{\text{vap}} = 85 \text{ J K mol}^{-1}$$

Therefore the diversity in liquids properties is dominated by the **ENTHALPY** of vaporization

### Enthalpies of Vaporization

Water	40.65 kJ mol <sup>-1</sup>
Ammonia	23.35 kJ mol <sup>-1</sup>
Diethyl Ether	27.4 kJ mol <sup>-1</sup>
Methane	8.19 kJ mol <sup>-1</sup>
Methanol	37.8 kJ mol <sup>-1</sup>
Ethanol	38.5 kJ mol <sup>-1</sup>
Propanol	47.5 kJ mol <sup>-1</sup>
Butanol	51.6 kJ mol <sup>-1</sup>

Why does butanol ( $C_4H_9OH$ ) have a lower vapor pressure than methanol ( $CH_3OH$ )?

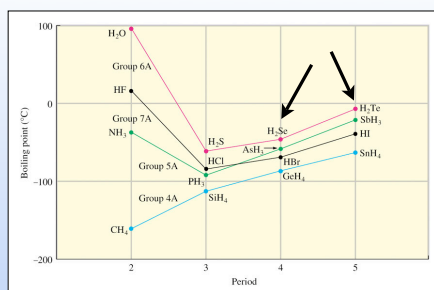
- A. it has a higher entropy
- B. it has stronger inter molecular forces
- C. it has a lower molecular weight
- D. it has a higher density

Intermolecular forces lead to the enthalpy difference between the liquid and the vapor

The larger the IMF the larger the  $\Delta H_{vap}$

The larger the  $\Delta H_{vap}$  the smaller the vapor pressure

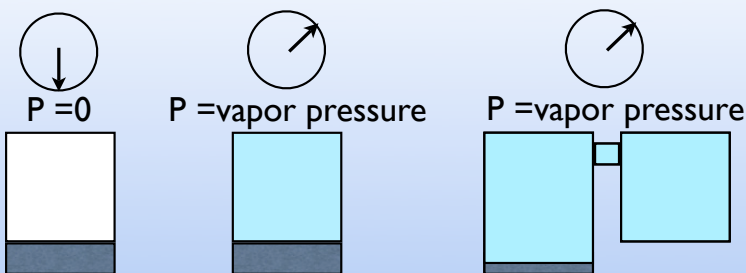
The the smaller the vapor pressure the higher the boiling point



Why is the boiling point of  $H_2Te$  higher than  $H_2Se$ ?

- A.  $H_2Te$  has a larger dipole
- B.  $H_2Se$  has more dispersion forces
- C.  $H_2Te$  has more dispersion forces
- D. Both A & C

Before we get to boiling let's look at how different properties affect vapor pressure



first all liquid

then comes to equilibrium with liquid + vapor with a pressure that is the vapor pressure

then add more volume  
At equilibrium there is less liquid, but the same Pressure!

### Quick Quiz

You have two containers.  
one has a total volume of 2 L and  
one has a total volume of 1 L  
Into each you place 500 mL of liquid ether  
They have the same temperature



Which container has a higher pressure at equilibrium?

- A. the 2 L container
- B. the 1 L container
- C. they are exactly the same ←
- D. it depends on the temperature

### What do you remember from last time?

You have two containers  
one has a total volume of 2 L and  
one has a total volume of 1 L  
Into each you place 500 mL of liquid ether



Which container has a greater number of ether molecules in the gas phase at equilibrium?

- A. the 2 L container ←
- B. the 1 L container
- C. they are exactly the same
- D. it depends on the temperature