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

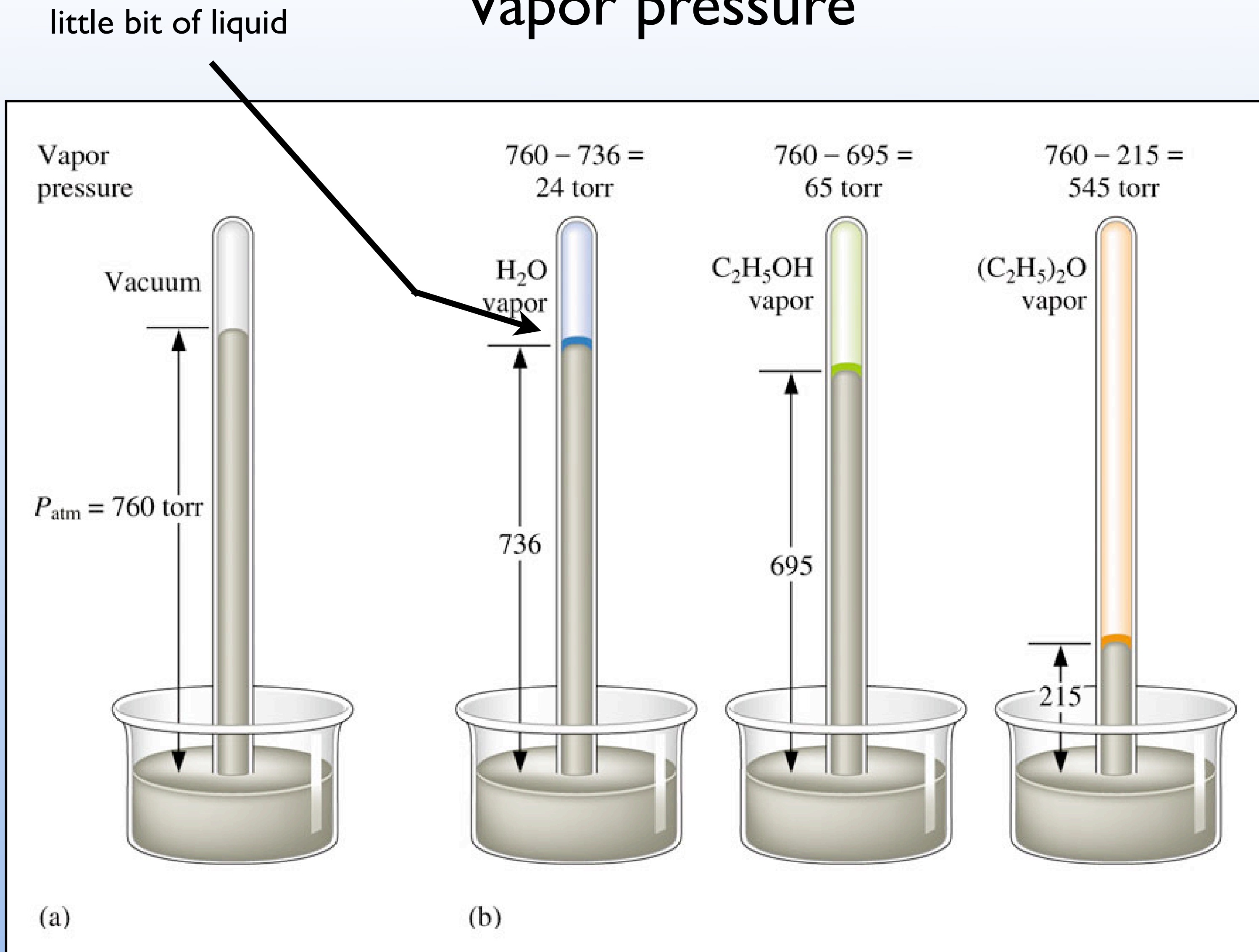
Phase transitions (no "chemistry")

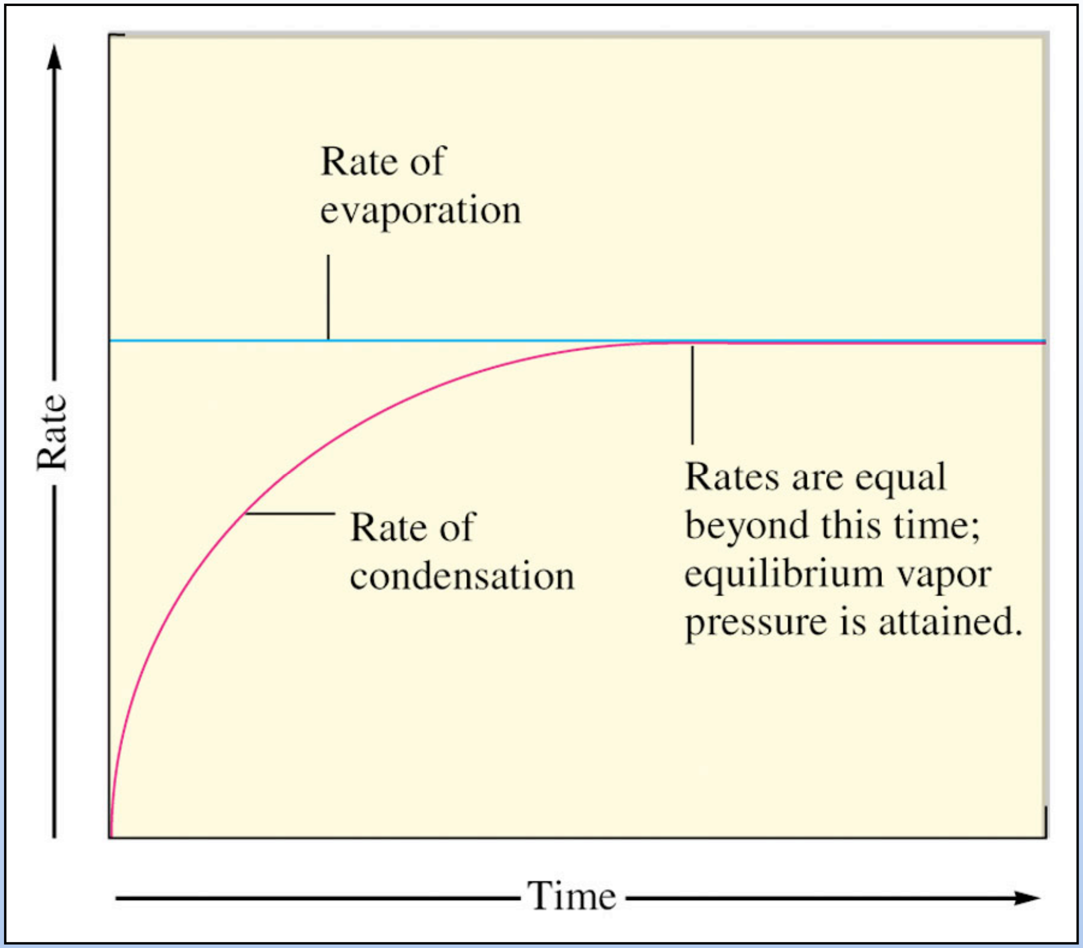
State with the lowest free energy is most stable

$$G = H - TS$$

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

Vapor pressure





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!

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

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

Enthalpies of Vaporization

Water	40.65 kJ mol^{-1}
Ammonia	23.35 kJ mol^{-1}
Diethyl Ether	27.4 kJ mol^{-1}
Methane	8.19 kJ mol^{-1}
Methanol	37.8 kJ mol^{-1}
Ethanol	38.5 kJ mol^{-1}
Propanol	47.5 kJ mol^{-1}
Butanol	51.6 kJ mol^{-1}

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

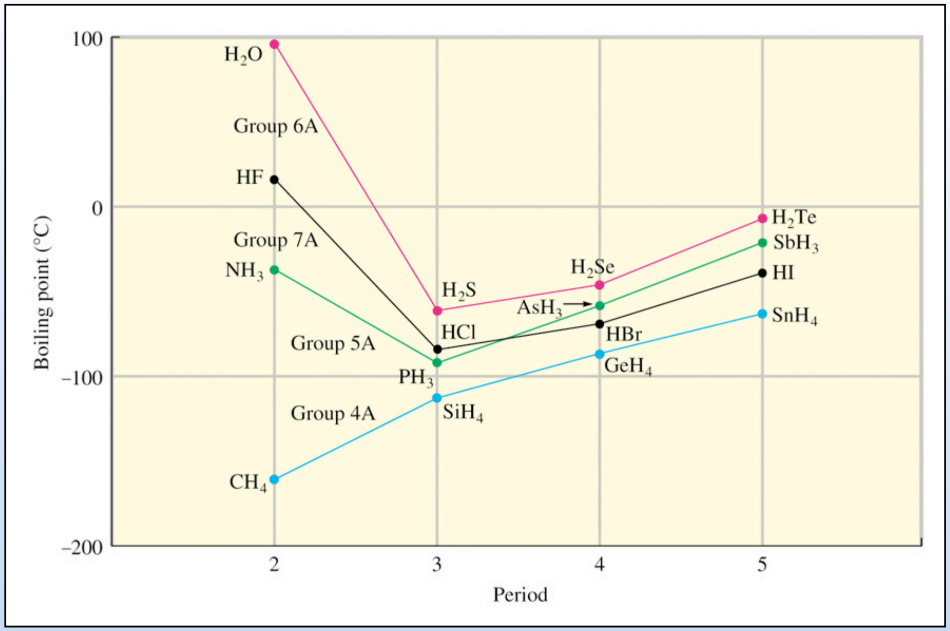
D. it has a higher density

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

The larger the IMF the larger the ΔH_{vap}

The larger the ΔH_{vap} the smaller the vapor pressure

The the smaller the vapor pressure the higher the boiling point



Why is the boilng point of H_2Te higher than H_2Se?

A. H_2Te has a larger dipole

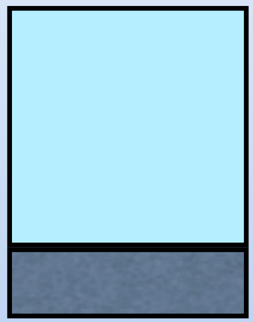
B. H_2Se has more dispersion forces

C. H_2Te has more dispersion forces

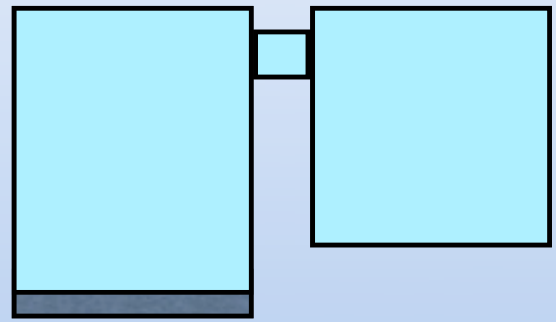
D. Both A & C

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!

At equilibrium $\Delta G = 0$

Therefore when a liquid is at its equilibrium vapor pressure

$$G_{gas} - G_{liq} = 0$$

The Gibbs energy of the liquid at a given pressure is essentially equal to the Gibbs Energy at standard pressure as it is a very weak function of pressure (know from Thermodyanamcis that is beyond what is covered in General Chemistry)

Therefore

$$G_{liq} = G^{o}_{liq}$$

The Gibbs energy of the gas is strong function of pressure such that (again a known thermodynamic result)

$$G_{gas} = G^{o}_{gas} + RT\ln P$$

Putting these two together we find

$$\Delta G = G_{gas} - G_{liq} = G^{o}_{gas} + RT\ln P - G^{o}_{liq} = 0$$
$$\Delta G^{o}_{VAP} = G^{o}_{gas} - G^{o}_{liq} = -RT\ln P$$

Where ΔG^{o}_{VAP} the standard Gibb's Energy for the reaction liq → gas and is given by

$$\Delta G^{o}_{VAP} = \Delta H^{o}_{VAP} - T\Delta S^{o}_{VAP}$$

Using all this we can relate the pressure to the temperature at equilibrium

$$\Delta G^{o}_{VAP} = \Delta H^{o}_{VAP} - T\Delta S^{o}_{VAP} = -RT\ln P$$
$$-\ln P = \frac{\Delta H^{o}_{VAP}}{RT} - \frac{\Delta S^{o}_{VAP}}{R}$$

This equation is essentially P as a function of T where all else is a constant. It is typically rearranged to look a two pressures P_2, and P_1 at two temperatures T_2 and T_1

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{o}_{VAP}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

This is the Claussius-Clapeyron Equation. It relates the vapor pressure at two temperature to the enthalpy of vaporization.