11/1/99

EXAM 2 — Results NOT GOOD

Some/much of the material that people did not understand is really essential stuff!

My policy of not curving stands — to do so would be to "dumb down" the course below what you all are capable of.

SOLUTION: NEXT MONDAY we will have an in-class exam to partially recover lost points. It will consist of a subset of the last exam, with perhaps some numbers changed.

Your score (fractional) will allow you to regain up to 50% of your missed points.

eg. Initial score 65/100
New score 80/100

Recovered $\frac{1}{2}(100-65)(\frac{80}{100}) = 14$

New score = 65 + 14 = 79

EXAMS WILL BE POSTED ON WEB (WITH NO ANSWERS). STUDY THEM PRACTICE, PRACTICE...

KEY ISSUES

Activity coefficients of ions >1? <1?

Almost everyone answered this – WHY?

MASS and CHARGE balance – General Chemistry!

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$$
$$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$$

Charge Balance

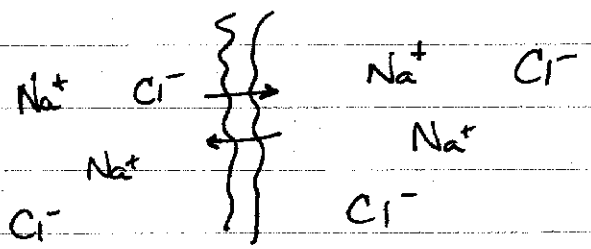
$$[H^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

but better

$$[H^+] = [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}] + [OH^-]$$

MASS BALANCE ⇐ BETTER: "MOLE BALANCE"

NaCl



EQUILIB REQUIRES →

$NaCl\,(IN) \rightarrow NaCl\,(out)$

Look at ~~equilibrium~~ chemical potential → that's G!

$$\mu^{IN}_{NaCl} = \mu^{\circ}_{NaCl} + RT \ln (a^{IN}_{Na^+})(a^{IN}_{Cl^-})$$

$$\mu^{OUT}_{NaCl} = \mu^{\circ}_{NaCl} + RT \ln (a^{OUT}_{Na^+})(a^{OUT}_{Cl^-})$$

See p. 212

$$\Delta G = \mu^{OUT}_{NaCl} - \mu^{IN}_{NaCl} =$$

$$= (RT \ln (a^{OUT}_{Na^+}\, a^{OUT}_{Cl^-})) - (RT \ln (a^{IN}_{Na^+}\, a^{IN}_{Cl^-}))$$

$$= RT \ln \frac{a^{OUT}_{Na^+}\, a^{OUT}_{Cl^-}}{a^{IN}_{Na^+}\, a^{IN}_{Cl^-}}$$

Colligative Properties

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

Effect of Pressure on $T_{boiling}$

remember normal boiling point is the temperature at which $P_s = 1$ atm

Assumes ΔH_{VAP} is independent of temperature

Previously $d\bar{G} = -\bar{S}dT + \bar{V}dP$

Effect of Pressure on $T_{melting}$

At the melting point, $d\bar{G}_l = d\bar{G}_s$ (in equilibrium)
(liquid-solid)

$$\therefore \quad -\bar{S}_s dT + \bar{V}_s dP = -\bar{S}_l dT + \bar{V}_l dP$$

$$-\bar{S}_s \frac{dT}{dP} + \bar{V}_s = -\bar{S}_l \frac{dT}{dP} + \bar{V}_l$$

$$(\bar{S}_l - \bar{S}_s)\frac{dT}{dP} = \bar{V}_l - \bar{V}_s$$

$$\Delta S_{fus} \frac{dT}{dP} = \Delta V_{fus}$$

$$\frac{dT}{dP} = \frac{\Delta V_{fus}}{\Delta S_{fus}}$$

Since, we're at equilib, the process is reversible

$$\Delta \bar{S}_{fus} = \frac{\Delta H_{fus}}{T}$$

$$\therefore \quad \frac{dT}{dP} = \frac{T\Delta V_{fus}}{\Delta H_{fus}}$$

$$\frac{\Delta T}{\Delta P} \approx \frac{T\,\Delta V_{fus}}{\Delta H_{fus}} \qquad \text{where } T \approx \frac{T_1 + T_2}{2}$$

Raoult's Law — Adding a solute to a solvent lowers the solvent's vapor pressure.

Why? → the solute lowers the total activity of the solvent

Vapor pressure is directly related to solvent activity.

$$P_A = X_A P_A^\circ$$

(P_A: vapor pressure; X_A: mole fraction of solvent; P_A°: vapor pressure of pure solvent)

Henry's Law — If the solute is volatile (eg mixing two solvents), then

More complicated. k_B varies for each system

$$P_B = k_B X_B$$

(P_B: vapor pressure of solute B; k_B: Henry's Law constant; X_B: mole fraction of B)

Boiling Point Elevation

$$T_b - T_o = K_b m$$

(T_b: new boiling temp; T_o: boiling temp of pure solvent; K_b: solvent-specific constant; m: molality of solute)

Freezing Point Depression

$$T_o - T_f = K_f m$$

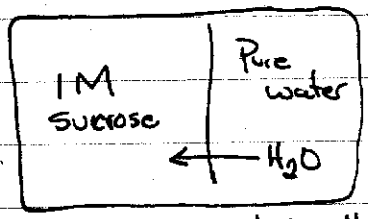
(T_o: freezing temp of pure solvent; T_f: new freezing temp; K_f: solvent-specific constant; m: molality of solute)

Conditions: 1) Dilute solution 2) Non-volatile solute

Molality ⇒ $\frac{\text{moles solute}}{1000\text{g solvent}}$

Osmotic Pressure

We've already seen a part of this



① Added solute lowers solvent activity

We've also seen that solvent activity correlates with vapor pressure. &

② Less solvent activity ⇒ lower vapor pressure

Therefore by reversal (Le'Chatelier) if we increase pressure, then we can (at least partially) reverse the effect of added solute and raise the solvent activity.