

Second Exam
March 4, 2009

First Page: Useful information and equations:

Law I $\Delta U = q + w$

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Law II: $dS = \frac{q_{rev}}{T}$

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

Comb I, II: $dU = TdS - PdV$

$$H = U + PV; \quad A = U - TS$$

$$G = H - TS; \quad dG = -SdT + VdP$$

Thermodynamic Equation of State

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}; \quad \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P;$$

$$\mu_A = \mu_A^\circ + RT \ln \frac{P_A}{P^\circ}$$

Dalton's and Raoult's Laws

$$P_A = \chi_A P_A^*; \quad P_A = y_A P_{Tot}; \quad P_A = \chi_A k_{H,A}$$

$$P_{Tot} = \sum_A P_A; \quad G = \sum n_i \mu_i$$

$$\Delta G_{mix} = RT \sum n_i \ln \left(\frac{P_i}{P^\circ} \right)$$

Integral Identity:

$$\Delta Z = \int_{x_i}^{x_f} \left(\frac{\partial Z}{\partial x} \right)_y dx$$

$$\text{Cyclic rule: } \left(\frac{dx}{dy} \right)_z \left(\frac{dz}{dx} \right)_y \left(\frac{dy}{dz} \right)_x = -1$$

Chain Rules:

$$\frac{d(yz)}{dx} = z \frac{d(y)}{dx} + y \frac{d(z)}{dx}$$

$$\frac{dx}{dz} = \frac{dy}{dz} \frac{dx}{dy}; \quad \left(\frac{\partial x}{\partial z} \right)_a = \left(\frac{\partial y}{\partial z} \right)_a \left(\frac{\partial x}{\partial y} \right)_a$$

$$\text{vdW Gas EoS: } P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

Reaction Info

$$\Delta H_{rxn}^\circ = \sum_i \nu_i \Delta H_f^\circ(i)$$

$$\Delta S_{rxn}^\circ = \sum_i \nu_i S_f^\circ(i)$$

$$dn_i = n_i - n_i^{init} = \nu_i dX$$

$$\Delta C_{p,rxn} = \sum_i \nu_i C_{p,m}(i)$$

$$\Delta H^\circ = \Delta H_{rxn}^\circ dX$$

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q_p = RT \ln \frac{Q_p}{K_p}$$

$$Q_p = \prod_{i=1}^N \left(\frac{P_i}{P^\circ} \right)^{\nu_i} \quad @ \text{Eq } Q_p = K_p$$

$$K_p = \left(\frac{P}{P^\circ} \right)^{\Delta \nu} \quad K_c = \left(\frac{c_o RT}{P^\circ} \right)^{\Delta \nu} K_p$$

Van't Hoff Eqn:

$$\ln \left(\frac{K_p(T_2)}{K_p(T_1)} \right) = - \frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Gas Constant:

$$R = 8.3 \text{ J / mol - K}$$

$$101 \text{ J} = 1 \text{ l - atm}$$

$$R = 0.082 \text{ l - atm / mol - K}$$

$$R \cdot 298.15 = 2.48 \text{ kJ / mol}$$

$$g = 9.8 \text{ m / sec}^2; \quad \rho_{(H_2O, \ell)} = 1 \text{ g/cc}$$

$$P = \rho gh$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$T(K) = T(C) + 273.15$$

Show your work throughout; clearly show what equations you are using, and always show units for computed quantities.

Name _____
ID _____

Q1) Consider the process where ice melts to liquid water at 0C and 1 atm. Estimate whether the thermodynamic quantities (listed below) are zero, greater than zero or less than zero for the system. Show your reasoning in a brief sentence for each quantity.

q , w , ΔV , ΔT , ΔP , ΔS , ΔU , ΔH , ΔA , ΔG .

The overall T does not change, the melting is endothermic (like boiling water) and it is at constant T and P.

Therefore **$\Delta T=0$** , **$\Delta P =0$**

Because ice floats on water the volume of the water decreases upon melting

$\Delta V < 0$

Being endothermic $q > 0$ and because the volume decreases **$w = -PdV > 0$** ., then the energy

$$\Delta U = q + w > 0$$

And because this is a change at constant P: **$\Delta H = q_p = q > 0$**

Because this is a reversible process at constant T and P **$\Delta G = 0$**

Finally the Helmholtz energy is the work which is positive so

$$dA = -SdT - PdV = w > 0$$

Q2) Diamonds are routinely made synthetically (usually for industrial purposes). Here is the chemical information about the reaction: $C(\text{graphite, solid}) \rightleftharpoons C(\text{diamond, solid})$

| | ΔH_f^0 kJ/mole | ΔG_f^0 kJ/mole | S_f^0 J/mole-K | ρ (g/cc) | C_p^0 J/mole-K |
|----------|------------------------|------------------------|------------------|---------------|------------------|
| Graphite | 0 | 0 | 5.74 | 1.8 | 8.52 |
| Diamond | 1.89 | 2.90 | 2.38 | 3.5 | 6.12 |

a) Is the above process spontaneous under standard conditions (25C, 1Atm)?

Demonstrate your answer based on calculation.

$$\Delta G_{rxn}^0 = \Delta G_{rxn}^0(\text{dia}) - \Delta G_{rxn}^0(\text{gra}) = 2.9 \text{ kJ/mole}$$

The reaction is NOT spontaneous at room temperature. Diamonds are not forever.

b) To make diamonds in the laboratory, graphite is subjected to 1500°C and $5 \cdot 10^4 \text{ Atm}$.

What is the $\Delta \bar{G}$ for this reaction at the high temperature and pressure? You may assume the entropy and density are independent of T and P for this purpose. Please, clearly show where you begin your calculation.

$$dG = -SdT + VdP \quad d\Delta G \uparrow = -\Delta SdT + \Delta VdP$$

$$\Delta G \uparrow = -\int_{T_0}^T \Delta SdT + \int_{P_0}^P \Delta VdP = -\Delta S\Delta T + \Delta V\Delta P$$

$$\Delta T = 1200\text{K} \quad \Delta S = (2.38 - 5.74) = -3.36 \text{ eu} \quad \Delta P = 5 \cdot 10^4 - 1 = 5 \cdot 10^4 \text{ Atm}$$

$$\Delta V = \left(\frac{1}{3.5} - \frac{1}{1.8} \right) \text{ cc/g} \cdot 1 \cdot 10^{-3} \text{ l/cc} \cdot 12 \text{ g/mole} = -0.0032 \text{ l/mole}$$

$$\Delta G \uparrow = -\Delta S\Delta T + \Delta V\Delta P = (3.36 \cdot 1.2 - 3.2 \cdot 5) = -12 \text{ kJ/mole}$$

$$\Delta G(T, P) = \Delta G(T_0, P_0) + \Delta G \uparrow = 2.9 - 12 = -9 \text{ kJ/mole}$$

c) If the entropy does depend on the T and P, estimate the entropy, $\Delta \bar{S}$, for this process at the high T and P. You may assume that the heat capacities and densities are

independent of P and T, and use the estimate that $\left(\frac{\partial V}{\partial T} \right)_P \approx \frac{\Delta V}{\Delta T}$. Please, be clear on what

equations you are using to start you calculation.

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad \Delta C_p = -2.4 \text{ J/K-mol}$$

$$\Delta S = \int dS = \int_{T_0}^T \left(\frac{\partial S}{\partial T} \right)_P dT + \int_{P_0}^P \left(\frac{\partial S}{\partial P} \right)_T dP = \int dS = \int_{T_0}^T \frac{\Delta C_p}{T} dT - \int_{P_0}^P \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$\Delta S = \int_{T_0}^T \frac{\Delta C_p}{T} dT - \int_{P_0}^P \left(\frac{\partial V}{\partial T} \right)_P dP = \Delta C_p \ln \frac{T}{T_0} - \left(\frac{\Delta V}{\Delta T} \right)_P \Delta P = -2.4 \ln \frac{15}{3} + \frac{3.2}{1.2} \cdot 5 = -3.8 + 13.3 = +10 \text{ eu}$$

This approximation makes the entropy change positive; the more exact correction for the second term makes it very small, still negative.

Q3) The Henry's law constants for oxygen and nitrogen in water are

$$k_H(N_2) = 9 \cdot 10^4 \text{ bar} \text{ and } k_H(O_2) = 5 \cdot 10^4 \text{ bar}.$$

a) Oxygen toxicity for divers occurs when the oxygen (partial) pressure exceeds 1.5 Atm. determine the maximum non-toxic depth one can go to using compressed air (which is 80/20 N₂/O₂).

$$P = P_0 + \rho gh = \left(1 + \frac{h}{32}\right)$$

$$P_{O_2} = 1.5 = .2 \left(1 + \frac{h}{32}\right) \quad \text{or} \quad \rho gh = 1 \frac{\text{kg}}{\ell} \cdot 9.8 \frac{\text{m}}{\text{sec}} \cdot 1 \cdot 10^3 \frac{\ell}{\text{m}^3} \cdot h = 0.1 \frac{\text{Bar}}{\text{m}} \cdot h = \frac{h}{10}$$

$$h = 208 \text{ feet} = 65 \text{ m}$$

b) At a depth of 200 feet (62 meters) how much nitrogen is dissolved in the blood? (Assume the values of the constants governing the solution of nitrogen and oxygen in blood are the same as the values in water.)

$$\chi = \frac{P_{N_2}}{k_H(N_2)} = \frac{yP_{Tot}}{k} = \frac{0.8 \cdot 7.2}{9 \cdot 10^4} = 0.064 \cdot 10^{-3} \approx \frac{n_{N_2}}{n_w} = [N_2] \bar{V}_w$$

$$[N_2] = 55 \cdot 0.064 \cdot 10^{-3} = 3.5 \text{ mM}$$

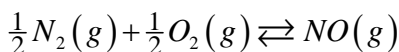
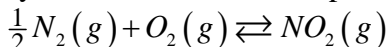
c) If the diver (from part b) surfaces rapidly, what volume of nitrogen would be generated when he reaches the surface, as gas bubbles in the blood? (Assume 5 liters of blood in the human body.)

There are 17mmoles of N₂ in the blood. So at the surface 1 Atm, 25C, that would

$$\text{occupy a volume of: } V = \frac{nRT}{P} = \frac{17 \cdot 10^{-3} \cdot .082 \cdot 300}{1} = 0.4 \ell, \text{ of course a small amount of}$$

that would still be soluble and would not come out. The amount that would remain dissolved would be at 1 Atm (vs 7.2 Atm) 0.05 liters.

Q4) An unwanted by product of gasoline combustion in a car is the generation of NO_x as the engine explosively burns hydrocarbons. Thus two possible reactions are written as:



The generation of these compounds comes about in the engine where (to a first approximation) air flows into the piston, the valves close, and the gas is compressed to about 10^{th} its initial volume. At this point the spark plug heats the mixture to about 2,000 degrees (Kelvin, as if it mattered). [The gas is cooled so fast that the amount of NO_x formed at high temperatures is kinetically trapped.]

| | ΔH_f^0 kJ/mole | ΔG_f^0 kJ/mole | S_f^0 J/mole-K | C_p^0 J/mole-K |
|---------------|------------------------|------------------------|------------------|------------------|
| O_2 | 0 | 0 | 205.2 | 29.4 |
| N_2 | 0 | 0 | 191.6 | 29.1 |
| NO | 91.3 | 87.6 | 210.8 | 29.9 Rxn 2 |
| NO_2 | 33.2 | 51.3 | 240.0 | 37.2 Rxn 1 |

a) Under these conditions NO_x can be formed. Assume the enthalpy and entropy are temperature independent (I know it is a stretch). Demonstrate whether either of the two gases can be formed at the high temperature and pressure, and which one is “more likely” to form.

$$\Delta S_{rxn1}^0 = 240 - 191.6 / 2 - 205.2 = -60 \text{ eu}$$

$$\Delta S_{rxn2}^0 = 210.8 - (191.6 + 205.2) / 2 = +12.4 \text{ eu}$$

$$\Delta G_{rxn1} = \Delta H_{rxn1}^0 - T \Delta S_{rxn1}^0 = 33.2 + 2 \cdot 60 = 150 \text{ kJ/mole}$$

$$\Delta G_{rxn2} = \Delta H_{rxn2}^0 - T \Delta S_{rxn2}^0 = 91.3 - 2 \cdot 12.4 = 66.5 \text{ kJ/mole}$$

The formation of NO is more plausible, while still not spontaneous under standard concentration conditions, the ΔG_{rxn} for it is much closer to zero and negative.

As a comment: Notice for NO production the temperature correction to ΔH and ΔS are indeed very small; eg. $\Delta C_p \Delta T \sim 1 \text{ kJ}$.

Alternatively, we can use the van't Hoff formulation to correct for the temperature as applied to reaction two (for the NO formation).

$$\ln K(T_0) = -\frac{\Delta G}{RT_0} = -\frac{87.6}{2.48} = -35.3$$

$$\ln \frac{K(T)}{K(T_0)} = \frac{\Delta H^0}{RT_0} \cdot \frac{\Delta T}{T} = \frac{91.3}{2.48} \cdot \frac{1700}{2000} = 31.3$$

$$-\frac{\Delta G}{RT} = \ln K(T) = \ln \frac{K(T)}{K(T_0)} + \ln K(T_0) = 31.3 - 35.3 = -4.0$$

$$\Delta G = 4 \cdot RT = 4 \cdot 8.3 \cdot 2 = 66 \text{ kJ/mole}$$

b) Let us focus on production of NO. How many moles of NO are formed from a single piston firing once? Assume a piston, of 0.5 liters, fills with air (80% N₂ and 20% O₂) at 1 Atm, and is then compressed to .05 liters (a 10 to 1 compression is typical) and then heated to 2000K, and that the residence time under these conditions is sufficient to achieve equilibrium (neglect the consumption of O₂ due to gas burning). [Running a car under typical conditions would have 8,000 such events per minute.] You may treat the gases as ideal gases. Make simplifying mathematical assumptions, if you wish, to streamline finding an answer.

$$K_p = Q_p = \exp\left(\frac{-\Delta G_{rxn}}{RT}\right) = 0.018 \quad Q_p = \frac{P_{NO}}{\sqrt{(P_N P_O)}}$$

$$n_N = 0.8 \frac{P_o V_o}{RT_o}$$

$$P_N = \frac{n_N RT}{V} = 0.8 \frac{RT}{V} \frac{P_o V_o}{RT_o} = 0.8 \frac{2000}{300} \frac{.5}{.05} \cdot 1 = 53 \text{Atm}$$

$$P_O = 14 \text{Atm}$$

$$P_N = P_N^0 - \frac{1}{2} P_{NO}$$

$$P_O = P_O^0 - \frac{1}{2} P_{NO}$$

$$P_{NO} = K_p \sqrt{\left(P_N^0 - \frac{1}{2} P_{NO}\right) \left(P_O^0 - \frac{1}{2} P_{NO}\right)} \approx K_p \sqrt{(P_N P_O)} = 0.018 \cdot 27 = 0.5$$

$$P_{NO} \approx .5 \text{Atm}$$

$$n_N = \frac{P_{NO} V}{RT} = \frac{0.5 \cdot 0.05}{0.082 \cdot 2 \cdot 10^3} = 0.15 \text{ m moles}$$