

CHM 3400 – Fundamentals of Physical Chemistry
Final Exam

Do the following problems. Show your work.

$R = 0.082057 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$	$N_A = 6.022 \times 10^{23}$
$R = 0.083145 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$	$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$
$R = 8.3145 \text{ J}/\text{mole}\cdot\text{K}$	$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$
$F = 96485. \text{ C}/\text{mol}$	$1 \text{ atm} = 760 \text{ torr}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$	$1 \text{ cm}^{-1} = 1.986 \times 10^{-23} \text{ J}$
$c = 2.998 \times 10^8 \text{ m}/\text{s}$	$1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
$m_e = 9.109 \times 10^{-31} \text{ kg}$	$1 \text{ amu} = 1.661 \times 10^{-27} \text{ kg}$
$R_\infty = 109737. \text{ cm}^{-1}$	
$R_H = 109678. \text{ cm}^{-1}$	

1. (32 points) Consider a real substance whose pressure and volume at a fixed temperature are related by the following equation of state

$$p = (a_1/V) + (a_2/V^2) \quad (1.1)$$

where a_1 and a_2 are constants.

a) The isothermal compressibility, κ , is defined as follows

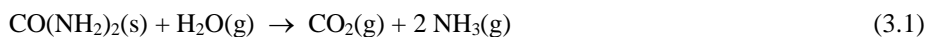
$$\kappa = - (1/V) (\partial V/\partial p)_T = - [V (\partial p/\partial V)_T]^{-1} \quad (1.2)$$

Find an expression for κ for a substance obeying the equation of state in eq 1.1.

b) Find an expression for w , the work, when the above substance is compressed isothermally and reversibly from an initial volume V_i to a final volume V_f .

2. (40 points) One mole of an ideal gas is expanded isothermally and irreversibly against a constant external pressure $p_{\text{ex}} = 2.00 \text{ atm}$. The initial and final volumes of the gas are $V_i = 2.00 \text{ L}$ and $V_f = 5.00 \text{ L}$, and the temperature of the gas is $T = 400.0 \text{ K}$. The constant pressure molar heat capacity of the gas is $C_{p,m} = 34.86 \text{ J}/\text{mol}\cdot\text{K}$. What are q , w , ΔU , ΔH , ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} for the above process? If there is not sufficient information to calculate one or more of the above quantities briefly explain what information is missing that prevents a value for the quantity from being found.

3. (32 points) A major source for ammonia (NH_3) in the lower atmosphere of the Earth is the hydrolysis of urea ($\text{CO}(\text{NH}_2)_2$). The hydrolysis reaction may be written



a) What are the numerical values for $\Delta G^\circ_{\text{rxn}}$, $\Delta H^\circ_{\text{rxn}}$, $\Delta S^\circ_{\text{rxn}}$, and K_{eq} for reaction 3.1 at $T = 25. \text{ }^\circ\text{C}$?

b) Give the expression for K_{eq} for the above reaction in terms of reactant and product activities, and the expression this reduces to for ideal behavior.

c) Will the value for K_{eq} increase, decrease, or stay the same as temperature increases? Give a valid justification for your answer.

Substance	M (g/mol)	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
$\text{CO}_2(\text{g})$	44.01	- 393.51	- 394.36	213.74	37.11
$\text{CO}(\text{NH}_2)_2(\text{s})$	60.06	- 333.51	- 197.33	104.60	93.14
$\text{H}_2\text{O}(\text{g})$	18.02	- 241.82	- 228.57	188.83	33.58
$\text{NH}_3(\text{g})$	17.03	- 46.11	- 16.45	192.45	35.

4. (24 points) Consider a sample of sulfur dioxide (SO_2) gas in equilibrium with aqueous sulfur dioxide at $T = 25.^\circ\text{C}$. When the partial pressure of SO_2 in the gas phase is $p(\text{SO}_2) = 0.0100 \text{ atm}$ the equilibrium concentration of dissolved SO_2 in water is $[\text{SO}_2] = 0.0124 \text{ mol/L}$. Based on this information find the following

a) K_B , the Henry's law constant for sulfur dioxide dissolved in water. Give your answer in units of torr. Note that at $25.^\circ\text{C}$ the density of water is $\rho = 1.00 \text{ g/mL}$.

b) The numerical value for K_{eq} , for the process



5. (20 points) The gas phase reaction of methane (CH_4) with hydroxyl radical (OH) is the initial step in the conversion of methane into carbon dioxide and water in the atmosphere of the Earth. The reaction is



The experimental value for the rate constant for reaction 5.1 is $1.5 \times 10^{-15} \text{ cm}^3/\text{molecule}\cdot\text{s}$ at $T = 240. \text{ K}$ and $6.4 \times 10^{-15} \text{ cm}^3/\text{molecule}\cdot\text{s}$ at $T = 300. \text{ K}$. What are A and E_a for the above reaction.

6. (16 points) When the sun is directly overhead, the Earth receives $1367. \text{ J}$ of energy every second for every square meter of surface area. Assuming that all of this energy is in the form of photons of yellow light ($\lambda = 580. \text{ nm}$) determine how many photons from the sun strike a 1.00 m^2 area of the Earth's surface every second.

7. (36 points) The diatomic molecule O_2 is an essential gas in the atmosphere of the Earth. For oxygen to be used in metabolism requires breaking the covalent bond in O_2 .

a) Experimentally, the vibrational constant for $^{16}\text{O}_2$ is $\omega = 1580. \text{ cm}^{-1}$. Based on this, and the mass of a ^{16}O atom ($m(^{16}\text{O}) = 15.9949 \text{ amu}$) find the value for k , the force constant in $^{16}\text{O}_2$.

b) Give the electron configuration and the number of unpaired electron spins for the following

- i. O (an oxygen atom)
- ii. O_2 (an oxygen molecule)
- iii. O_2^- (the oxygen molecule anion)

Solutions.

$$1) \quad a) \quad \kappa = - \left[V \left(\frac{\partial p}{\partial V} \right)_T \right]^{-1}$$

$$\text{But } \left(\frac{\partial p}{\partial V} \right)_T = \frac{\partial}{\partial V} \left[\left(\frac{a_1}{V} \right) + \left(\frac{a_2}{V^2} \right) \right] = - \left(\frac{a_1}{V^2} \right) - \frac{2a_2}{V^3} = - \frac{(2a_2 + a_1 V)}{V^3}$$

$$\text{So } \kappa = - \left\{ V \left[- \frac{(2a_2 + a_1 V)}{V^3} \right] \right\}^{-1} = \left[\frac{(2a_2 + a_1 V)}{V^2} \right]^{-1} = \frac{V^2}{(2a_2 + a_1 V)}$$

$$b) \quad w = - \int_i^f p_{\text{ex}} dV. \quad \text{The process is reversible, and so } p_{\text{ex}} = p.$$

$$\text{So } \quad w = - \int_i^f \left[\left(\frac{a_1}{V} \right) + \left(\frac{a_2}{V^2} \right) \right] dV \\ = - \left\{ a_1 \ln(V_f/V_i) - a_2 \left[\left(\frac{1}{V_f} \right) - \left(\frac{1}{V_i} \right) \right] \right\}$$

2) The process is isothermal and the gas is ideal, and so $\Delta U = \Delta H = 0$.

$$\Delta U = q + w = 0, \text{ and so } q = -w$$

$$w = - \int_i^f p_{\text{ex}} dV \quad \text{The process takes place against a constant external pressure, and so}$$

$$w = - p_{\text{ex}} \int_i^f dV = - p_{\text{ex}} (V_f - V_i) = - (2.00 \text{ atm}) [(5.00 \text{ L}) - (2.00 \text{ L})] \\ = - 6.00 \text{ L}\cdot\text{atm} (101.3 \text{ J/1 L}\cdot\text{atm}) = - 608. \text{ J} \quad (\text{and so } q = + 608. \text{ J})$$

$$\Delta S_{\text{surr}} = - q_{\text{sys}}/T = (- 608. \text{ J})/(400. \text{ K}) = - 1.52 \text{ J/K}$$

For ΔS_{sys} we need a reversible process with the same initial and final state as the actual process taking place. One such pathway is the isothermal reversible expansion of the gas from an initial volume $V_i = 2.00 \text{ L}$ to a final volume $V_f = 5.00 \text{ L}$, at a constant temperature $T = 400. \text{ K}$. Since the process is isothermal and the gas is ideal

$$\Delta U = q + w = 0, \text{ and so } q = -w$$

$$w = - \int_i^f p_{\text{ex}} dV \quad \text{For a reversible process on an ideal gas, } p_{\text{ex}} = p = nRT/V.$$

$$\text{So } \quad w = - \int_i^f (nRT/V) dV = - nRT \ln(V_f/V_i)$$

$$q = -w = nRT \ln(V_f/V_i)$$

$$\Delta S_{\text{sys}} = \int_i^f (dq_{\text{rev}}/T) = (1/T) \int_i^f dq_{\text{rev}} = q_{\text{rev}}/T = [nRT \ln(V_f/V_i)]/T = nR \ln(V_f/V_i) \\ = (1.00 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K}) \ln(5.00/2.00) = + 7.62 \text{ J/K}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 7.62 \text{ J/K} + (- 1.52 \text{ J/K}) = + 6.10 \text{ J/K}.$$

$$3) \quad a) \quad \Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_f(\text{CO}_2(\text{g})) + 2 \Delta G^\circ_f(\text{NH}_3(\text{g}))] - [(\Delta G^\circ_f(\text{CO}(\text{NH}_2)_2(\text{s})) + \Delta G^\circ_f(\text{H}_2\text{O}(\text{g})))]$$

$$= [(- 394.36) + 2 (- 16.45)] - [(- 197.33) + (- 228.57)] = - 1.36 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = [\Delta H^\circ_f(\text{CO}_2(\text{g})) + 2 \Delta H^\circ_f(\text{NH}_3(\text{g}))] - [(\Delta H^\circ_f(\text{CO}(\text{NH}_2)_2(\text{s})) + \Delta H^\circ_f(\text{H}_2\text{O}(\text{g})))]$$

$$= [(- 393.51) + 2 (- 46.11)] - [(- 333.51) + (- 241.82)] = -89.60 \text{ kJ/mol}$$

$$\Delta S^\circ_{\text{rxn}} = [S^\circ(\text{CO}_2(\text{g})) + 2 S^\circ(\text{NH}_3(\text{g}))] - [S^\circ(\text{CO}(\text{NH}_2)_2(\text{s})) + S^\circ(\text{H}_2\text{O}(\text{g}))]$$

$$= [(213.74) + 2 (192.45)] - [(104.60) + (188.83)] = 305.21 \text{ J/mol}\cdot\text{K}$$

$$\ln K_{\text{eq}} = - \Delta G^\circ_{\text{rxn}} / RT = - (-1360. \text{ J/mol}) / [(8.314 \text{ J/mol}\cdot\text{K})(298. \text{ K})] = 0.549$$

$$K_{\text{eq}} = e^{0.549} = 1.73$$

$$\text{b) } K_{\text{eq}} = \frac{(a_{\text{CO}_2})(a_{\text{NH}_3})^2}{(a_{\text{CO}(\text{NH}_2)_2})(a_{\text{H}_2\text{O}})} \cong \frac{(p_{\text{CO}_2})(p_{\text{NH}_3})^2}{(p_{\text{H}_2\text{O}})}$$

c) From the Le Chatelier principle, for an endothermic reaction increasing the temperature increases the concentrations of products and decreases the concentrations of reactants. Therefore, as T increases, K_{eq} increases.

4) a) Henry's law says $p_B = K_B X_B$,

$$\text{so } K_B = p_B / X_B$$

Assume 1.00 L solution, and that the density of the solution is the same as the density of water. Then

$$\text{mol SO}_2 = 0.0124 \text{ mol}$$

$$\text{mol H}_2\text{O} = 1000. \text{ g} (18.01 \text{ g/1. mol}) = 55.52 \text{ mol H}_2\text{O}$$

$$X_B = \frac{(0.0124)}{(55.52 + 0.0124)} = 2.23 \times 10^{-4}$$

$$K_B = \frac{(0.0100 \text{ atm})}{2.23 \times 10^{-4}} \frac{760. \text{ torr}}{1 \text{ atm}} = 3.40 \times 10^4 \text{ torr}$$

b) For reaction 4.1

$$K_{\text{eq}} = \frac{(a_{\text{SO}_2(\text{aq})})}{(a_{\text{SO}_2(\text{g})})} \cong \frac{[\text{SO}_2]}{p_{\text{SO}_2}} = \frac{0.0124}{0.01013} = 1.22$$

Note that we expressed the pressure in units of bar (standard units for gases).

5) Based on the Arrhenius equation we may say

$$\ln(k_2/k_1) = - (E_a/R) [(1/T_2) - (1/T_1)]$$

$$E_a = - \frac{R \ln(k_2/k_1)}{[(1/T_2) - (1/T_1)]} = - \frac{(8.314 \text{ J/mol}\cdot\text{K}) \ln(6.4 \times 10^{-5} / 1.5 \times 10^{-5})}{[(1/300. \text{ K}) - (1/240. \text{ K})]} = 14.47 \text{ kJ/mol}$$

$$k = A \exp(-E_a/RT)$$

$$A = k \exp(+E_a/RT)$$

If we use the value for k at T = 240. K

$$A = (1.5 \times 10^{-15} \text{ cm}^3/\text{molecule}\cdot\text{s}) \exp[(14470 \text{ J/mol}) / (8.314 \text{ J/mol}\cdot\text{K})(240. \text{ K})]$$

$$= 2.11 \times 10^{-12} \text{ cm}^3/\text{molecule}\cdot\text{s}$$

6) $E = N (hc/\lambda)$

So $N = \frac{E\lambda}{hc} = \frac{(1367. \text{ J})(580. \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})} = 3.99 \times 10^{21} \text{ photon}$

7) a) $\omega = \frac{1}{2\pi c} (k/\mu)^{1/2}$; so $k = 4\pi^2 c^2 \omega \mu$ $\omega = 1880. \text{ cm}^{-1} = 1.880 \times 10^5 \text{ m}^{-1}$

$$\mu = \frac{(15.9949 \text{ amu})(15.9949 \text{ amu})}{(15.9949 + 15.9949) \text{ amu}} = 7.9974 \text{ amu} \quad \frac{1.661 \times 10^{-27} \text{ kg}}{1 \text{ amu}} = 1.3284 \times 10^{-26} \text{ kg}$$

$$k = 4\pi^2 (2.998 \times 10^8 \text{ m/s})^2 (1.580 \times 10^5 \text{ m}^{-1})^2 (1.3284 \times 10^{-26} \text{ kg}) = 1177. \text{ N/m}$$

b) $\text{O } 1s^2 2s^2 2p^4$ # unpaired e- spins = 2

$\text{O}_2 (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (1\pi_u)^4 (1\pi_g^*)^2$ # unpaired e- spins = 2

$\text{O}_2^- (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (1\pi_u)^4 (1\pi_g^*)^3$ # unpaired e- spins = 1