57 pts

Duration: 80 minutes
Date: Oct. 31, 2012

CHM 2132
MidTerm exam

Name: ____________________
Student # ________________

Answer all questions.

1. The following parts to this question are designed to test you on a variety of physico-chemical concepts or as steps towards answering a larger question.

   a) An average person takes 18 breaths of air per minute into his lungs. A normal pair of lungs expands to a volume of 0.5 L. How many Litres of air does the person inhale (and therefore also exhale) per hour ?

$$V = 18 \times 0.5 \text{ L min}^{-1}$$
$$= 18 \times 0.5 \times 60 \text{ L h}^{-1}$$
$$= \boxed{540 \text{ L h}^{-1}}$$

2

   b) The exhaled air is almost saturated with water vapour at body temperature. The vapour pressure of water at 37 °C is 0.062 atm. What is the mass of water exhaled per day?

$$n = \frac{pV}{RT} = \frac{0.062 \text{ atm} \times 540 \text{ L h}^{-1}}{0.08216 \text{ L atm mol}^{-1}\text{K}^{-1} \times 310\text{K}} = 1.315 \text{ mol h}^{-1}$$
$$= 1.315 \times 24 \text{ mol day}^{-1}$$
$$= 1.315 \times 24 \times 18 \text{ g day}^{-1}$$
$$= \boxed{568 \text{ g day}^{-1}}$$

2

   c) If the person is breathing in air at 20C, where the equilibrium vapour pressure should be 0.023 atm, but the relative humidity is only 50%, how much water is inhaled, and therefore how much is lost per day via normal respiration?

$$p_{H_2O} = 0.023 \times 0.5 = 0.0115 \text{ atm}$$
$$n = \frac{0.0115 \text{ atm} \times 540 \text{ L h}^{-1}}{0.08216 \text{ L atm mol}^{-1}\text{K}^{-1} \times 293\text{K}} = 0.258 \text{ mol h}^{-1}$$
$$= 0.258 \times 24 \times 18 \text{ g day}^{-1}$$
$$= 111 \text{ g day}^{-1}$$
$$\text{Loss} = 568 - 111 = \boxed{457 \text{ g day}^{-1}}$$

3

d) Given that the standard molar enthalpies of formation of gaseous H_2O (18 g mol^{-1}), CO_2, and of aqueous sucrose, $C_{12}H_{22}O_{11}$ (342 g mol^{-1}), are -241.83 kJ mol^{-1}, –393.51 kJ mol^{-1}, and -2215.85 kJ mol^{-1} respectively, calculate the molar enthalpy of combustion of sucrose:

$$C_{12}H_{22}O_{11} + 12\,O_2 \rightarrow 12\,CO_2 + 11\,H_2O$$

Express the result also in units of kJ per g of water produced.

$$\Delta\bar{H}_r = 11(-241.83)+12(-393.51)-(-2215.85)$$
$$= \boxed{-5166.4\ \text{kJ mol}^{-1}}\ \text{of sucrose}$$

4

1 mole of sucrose produces 11 moles of H_2O, ie $11 \times 18 = 198$ g H_2O

$$\therefore \Delta\bar{H} = \frac{-5166.4\ \text{kJ mol}^{-1}\text{sucrose}}{198\ \text{g H}_2\text{O mol}^{-1}\ \text{sucrose}}$$
$$= \boxed{26.09\ \text{kJ g}^{-1}\ \text{of H}_2\text{O}}$$

e) Aside from respiration, other processes (perspiration and waste) also contribute to the total water loss. This is usually made up by drinking. In one particular case, a person did not drink enough, and so he lost 100 g of water per day. This must be made up by the internal combustion of his food (here considered to be aqueous sucrose). How much sucrose must he consume for this purpose? The caloric content of one apple is 72 "Calories". How many apples must he consume to make up for the water deficit?

3

1 g of H_2O is ~~associated~~ with 26.09 kJ
∴ 100 g of H_2O is associated with 2609 kJ

The caloric content of an apple = 72 kcal = 72000 × 4.184 J
= 301.0 kJ

∴ the number of apples needed = 2609 kJ/301 kJ apple = 8.67 apples

f) Not all of the energy calculated in part d) can be used to perform useful work. Why not? What is the ideal efficiency of the human body for the conversion of heat to work when the room temperature is 20 °C ? What assumption is implied in this calculation?

2

The second law of thermodynamics limits this to a maximum efficiency

$$e = (T_h - T_c)/T_h$$
$$= \frac{310-293}{310} = 0.0548 = 5.48\%$$

g) Use the two vapour pressures cited in parts b) and c) in order to determine the enthalpy of vaporization of water. What assumptions are implied in the calculation?

$P_2 = 0.062$ atm @ T_1: 37°c = 310K

$P_1 = 0.023$ atm @ T_2 = 20°c = 293K

5

$$\ln \frac{p_2}{p_1} = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{0.062}{0.023}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{310} - \frac{1}{293}\right)$$

$$0.9916 = -\frac{\Delta H_{vap}}{8.314}\left(-1.872 \times 10^{-4}\right)$$

$$\Delta H_{vap} = \frac{8.314 \times 0.9916}{1.872 \times 10^{-4}} = 44050$$

$$= \boxed{44.05 \text{ kJmol}^{-1}}$$

h) While the person is breathing in air, he is breathing in oxygen. The blood of a healthy person is analyzed and it is found that 1 L of blood has the capacity to dissolve 0.2 L of O_2 (measured at 298 K and 1 atm). What is oxygen's molar concentration in the blood, and what is its mole fraction? Assume that blood is essentially water for these purposes.

$V_{O_2} = 0.2L$

$$n_{O_2} = \frac{PV}{RT} = \frac{1 \text{ atm} \times 0.2L}{0.08216 \times 298} = 0.008169 \text{ mol}$$

$$\boxed{[O_2] = 8.169 \times 10^{-3} M}$$

4

$V_{H_2O} \simeq V_{solution} = 1 L$, $m_{H_2O} = 1000 g$

$$n_{H_2O} = \frac{1000 g}{18 g mol^{-1}} = 55.56 \text{ mol}$$

$$\therefore X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}} = \frac{8.169 \times 10^{-3}}{55.56 + 0.008} = \frac{8.169 \times 10^{-3}}{55.57} = \boxed{1.470 \times 10^{-4}}$$

i) Henry's law's constant for the volatility of oxygen in water is 42700 in atmosphere units. Use the answer in part h) to determine what the actual equilibrium partial pressure of oxygen could be for blood plasma (if blood were to be exposed to the atmosphere)?

2

Henry's law $P_{O_2} = k_H X_{O_2}$

$$= 42700 \times 1.470 \times 10^{-4}$$

$$= \boxed{6.28 \text{ atm}}$$

j) Oxygen is obviously not the only solute found in blood. The total concentration of all solutes is approximately 1 M. Use this value to

- calculate the mole fraction of water in blood and,

In 1 L of solution, $V_{H_2O} \simeq 1 L$

$$n_{H_2O} = \frac{1000\ g}{18\ g\,mol^{-1}} = 55.56\ mol$$

2

$$n_B = 1\ mol$$

$$\therefore X_{H_2O} = \frac{55.56}{55.56+1} = \boxed{0.9823}$$

- along with the data in part b) to calculate the partial pressure of water at 37 °C according to Raoult's law. By what amount does it differ from that of pure water?

<u>Raoult's law</u> $P_A = X_A P_A^{\circ}$

3

$$= 0.9823 \times 0.062$$

$$= \boxed{0.06090\ atm}$$

$$\Delta p = 0.06090 - 0.0620 = \boxed{-0.001096\ atm} = -0.833\ torr$$

- By how much does the chemical potential of water differ from that of pure water? Note that the activity coefficient for <u>water</u> (which we determined in the lecture notes) is 0.874 under these conditions.

$$\mu_A = \mu_A^{\circ} + RT \ln a_A$$

3

$$= \mu_A^{\circ} + RT \ln(\gamma_A X_A)$$

$$\Delta\mu = RT \ln(0.874 \times 0.9823)$$

$$= 8.314 \times 310 \times (-0.1525)\ J\,mol^{-1} = -393\ J\,mol^{-1}$$

- Estimate the value of the freezing point depression of blood.

$$\Delta T = -k_f m_B$$

2

$$\simeq -1.86 \times 1$$

$$\boxed{= -1.86\ ^{\circ}C}$$

$m_B \simeq 1 M$

(includes all electrolytes)

nonlinear $N=4$. $\bar{C}_V = \frac{3}{2}R + \frac{3}{2}R + (3N-6)R = \boxed{9R}$

2. One Litre of NH_3 (a pyramidal shaped molecule) is expanded to 2 L. The initial pressure is 1 atm, and the initial temperature is 25 °C. Calculate the final pressure and temperature, as well as q, w, ΔU, and ΔS for **EITHER** isothermal **OR** adiabatic expansion. **<u>Your choice</u>**. But for isothermal choice also calculate ΔG.

$\underline{\text{Isothermal}}$ $T_1 = T_2 = 298K$

$P_1 = 1 atm$

$V_1 = 1 L$

$V_2 = 2 L$

$n = \frac{PV_1}{RT_1} = \frac{1 \times 1}{0.08216 \times 298}$

$= 0.04084 \text{ mol}$

$\therefore \frac{P_2}{P_1} = \frac{V_1}{V_2} = \frac{1}{2}$ $\therefore P_2 = \frac{1}{2} \times 1 = \boxed{0.5 atm}$

$T_2 = \boxed{298 K}$

$\boxed{\Delta U = 0}$

$w = -nRT \ln \frac{V_2}{V_1} = -PV \ln \frac{V_2}{V_1} = -P_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$

$= -(1 atm)(1 L) \ln(2)$

$= -0.693 \text{ Latm}$

$= -0.693 \times 101.325$

$= \boxed{-70.22 J}$

$w = -nRT \ln 2$

$= 0.04084 \times 8.314 \times 298 \ln 2$

$= -70.14 J$

10

$q = \Delta U - w = 0 + \boxed{70.22 J}$

$\Delta S = nR \ln \frac{V_2}{V_1} + n\bar{C}_V \ln \frac{T_2}{T_1} = nR \ln \frac{V_2}{V_1}$

$= 0.04084 \times 8.314 \ln 2$

$= \boxed{0.235 JK^{-1}}$

$\Delta H = 0$

$\Delta G = \Delta H - \Delta(TS)$

$= 0 - T\Delta S$

$= -298 \times 0.235$

$= \boxed{-70.14 J}$

5b)

Adiabatic

$$\left.\begin{aligned} T_1 &= 298\,K \\ P_1 &= 1\,atm \\ V_1 &= 1L \\ V_2 &= 2L \end{aligned}\right\} \qquad n = \frac{P_1V_1}{RT_1} = \frac{1\times1}{0.08216\times298} = 0.04084 \text{ mol}$$

$$\bar{C}_V = \frac{3}{2}R + \frac{3}{2}R + (3N-6)R \qquad N = 4 \text{ for } NH_3 \text{ (nonlinear)}$$

$$= 3R + 6R$$

$$= 9R$$

$$\bar{C}_p = 10R$$

$$\gamma = \frac{\bar{C}_p}{\bar{C}_V} = \frac{10}{9} = 1.111$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} = (0.5)^{1.111} = 0.4629$$

$$P_2 = \boxed{0.4629} \text{ atm}$$

10

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \left(\frac{0.4629}{1}\right)\left(\frac{2}{1}\right) = 0.9259$$

$$T_2 = T_1\times0.9259 = 298\times0.9259 = \boxed{275.9\ K}$$

$$\Delta U = n\bar{C}_V\Delta T$$

$$= 0.04084\times9R\,(275.9-298)$$

$$= \boxed{-67.50\ J}$$

$$w = \Delta U - q$$

$$= \Delta U$$

$$= \boxed{-67.5\ J}$$

$$\Delta H = n\bar{C}_p\Delta T$$

$$= 0.04084\times10R\times(275.9-298)$$

$$= \boxed{-75.04\ J}$$

$\Delta S = \boxed{0}$ for adiabatic process

$$\Delta G = \Delta H - \Delta(TS)$$

$$= \Delta H - T_2\Delta S - S_2\Delta T$$

we don't know this value
so we can't calculate ΔG.

3. One of the major reactions accompanying oxidative phosphorylation that results in ATP formation in mitochondria is the oxidation of NADH. It is a redox reaction whose parts are as follows. The data are for 25 °C and correspond to the *chemical* standard state:

$$2\,H^+ + 2\,e^- + \tfrac{1}{2}\,O_2 \rightarrow H_2O \qquad \Delta\bar{G}^0 = -237.16\ kJ\ mol^{-1} \quad (1)$$

$$NAD^+ + H^+ + 2\,e^- \rightarrow NADH \qquad \Delta\bar{G}^0 = +20.26\ kJ\ mol^{-1} \quad (2)$$

a) Write down the overall reaction for the <u>oxidation</u> of NADH. Calculate the standard molar free energy change for the overall reaction at 25 °C. Will the reaction occur spontaneously? Explain.

$(1)-(2)$: $NADH + H^+ + \frac{1}{2}O_2 \rightarrow NAD^+ + H_2O$

$$\Delta\bar{G}^\circ = \Delta\bar{G}_1^\circ - \Delta\bar{G}_2^\circ = -237.16 - 20.26 = \boxed{-257.42}\ kJ\,mol^{-1}$$

2

$\Delta\bar{G}^\circ < 0$ ∴ spontaneous if all aqueous substances are in their standard states of 1M, and if $P_{O_2} = 1\,atm$

b) Calculate the corresponding equilibrium constant?

$$K = \exp\left(-\frac{\Delta\bar{G}^\circ}{RT}\right) = \exp\left(+\frac{257420}{8.314 \times 298}\right)$$

2

$$= e^{103.9}$$

$$= \boxed{1.328 \times 10^{45}}$$

c) Calculate the standard biochemical molar free energy change.

$$\Delta\bar{G}^{\circ\prime} = \begin{cases} \Delta\bar{G}^\circ - 39.9n\ kJ\,mol^{-1} \text{ for the production of } n\ H^+ \\ \Delta\bar{G}^\circ + 39.9n\ kJ\,mol^{-1} \text{ for the consumption of } n\ H^+ \end{cases}$$

3

Here 1 proton is consumed

$$\therefore \Delta\bar{G}^{\circ\prime} = -257.42 + 39.9 = \boxed{-217.52\ kJ\,mol^{-1}}$$

d) In mitochondria the actual concentrations are: [NADH] = 1 mM, [NAD^+] = 2 mM, $p_{O_2} = 0.1\ atm$. If the pH is 8 will the reaction occur spontaneously under these conditions?

3

$$\Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln\left(\frac{[NAD^+]}{[NADH][H^+]\,P_{O_2}^{1/2}}\right)$$

or $\Delta\bar{G}^{\circ\prime}$ with $\left(\frac{[H^+]}{10^{-7}}\right)$

$$= -257420 + 8.314 \times 298 \ln\left(\frac{2 \times 10^{-3}}{1 \times 10^{-3} \times 10^{-8} (0.1)^{1/2}}\right)$$

$$= -257420 + 2477.5 \ln(6.325 \times 10^{8}) = -257420 + 50208 = \boxed{-207.21\ kJ\,mol^{-1}}$$

spontan

$\ln P_{vap} = -\frac{\Delta \bar{H}_{vap}}{RT} + c$

$q_P = \Delta H$

$e = \frac{T_c - T_F}{T_c}$

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

$P_B = k_H X_B$

$P_A = X_A P_A^\circ$

$\mu_A = \mu_A^\circ + RT \ln a_A$

$a_i = \gamma_i X_i$

$\Delta T = -k_f m_B$

$$\bar{C}_V = \begin{cases} \frac{3}{2}R \\ \frac{3}{2}R + R + (3N-5)R \\ \frac{3}{2}R + \frac{3}{2}R + (3N-6)R \end{cases}$$

$\bar{C}_p = \bar{C}_V + R$

$w = -nRT \ln(V_2/V_1)$

$\Delta U = q + w$

$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) + n\bar{C}_V \ln\left(\frac{T_2}{T_1}\right)$

$\Delta \bar{U} = \bar{C}_V \Delta T$

$\Delta \bar{H} = \bar{C}_p \Delta T$

$G = H - TS$

$\gamma = \bar{C}_p / \bar{C}_V$

$P_2 V_2^\gamma = P_1 V_1^\gamma$ $\quad T_2/T_1 = (V_1/V_2)^{R/\bar{C}_V}$

$K = e^{-\Delta \bar{G}^\circ / RT}$

$\Delta \bar{G}^{\circ\prime} = \Delta \bar{G}^\circ \pm 39.9n$ kJ mol^{-1} $\quad \Delta \bar{G} = \Delta \bar{G}^\circ + RT \ln Q$

$R = 1.98 \frac{\text{cal}}{\text{mol K}} = 8.314 \frac{\text{J}}{\text{mol K}} = 0.08216 \frac{\text{L atm}}{\text{mol K}}$

1 atm = 760 mmHg = 101325 Pa

1 cal = 4.184 J

1 L atm = 101.325 J

$k_f(H_2O) = 1.86$ K kg mol^{-1}