YOUR NAME (last name, first name) ......ANSWERS........

ID# ....

WINTER 2019
MIDTERM

(Total number of pages = 10)

(Total points = 120)

(Total time = 120 mins)

YOUR DISCUSSION SECTION   ....

YOUR TA   ……………………….

Write in pen.

Do not use white-out.

This is a closed book exam.

You must show all your work.

Check your units and significant figures.

See last page for constants and equations.

BOX FINAL ANSWERS

Think Clearly   Good Luck

Do not write on this page.

QUESTION	SCORE
1	
2	
3	
4	
5	
6	
7	
8	
TOTAL	

Q1. Sulfur dioxide is produced as a by-product of the burning of fossil fuels contaminated with sulfur compounds. Sulfur dioxide can further react with more molecular oxygen to form sulfur trioxide which is a significant pollutant contributing to acid rain.

A. The equilibrium constant, K_P, for the unbalanced reaction $SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons SO_{3\,(g)}$ at 700 K is 3×10^4. A mixture of SO_2, O_2, and SO_3, each at 65 bars was introduced into a reaction container at 700 K. Is the reaction at equilibrium? If not, does SO_3 tend to form or decompose?   (8pt)

   $2\,SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2\,SO_{3\,(g)}$ 2pt

   $$Q_p = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = \frac{(65\,bar)^2}{(65\,bar)^2(65\,bar)} = 2 \times 10^{-2}$$

   1pt   1pt

   $\therefore Q_P \neq K_P \Rightarrow$ the reaction is not at equilibrium.   2pt

   Since $Q_P < K_P$, $\therefore$ The reaction has a tendency to proceed toward SO_3.   2pt

B. For the above reaction, if the volume of the reaction container is reduced will the forward or reverse reaction be favored?   (2pt)

   Forward reaction is favored.

C. Using the data given in part A comment on the relative stability of the reactants and products.   (2pt)

   Equilibrium constant is large, therefore, the product, SO_3, is more stable.

Q2. Ammonia, NH_3, is a common nitrogenous waste, particularly among aquatic organisms. You are studying the following unbalanced reaction at high temperatures to determine ammonia's stability in the gas phase:

$$NH_{3\,(g)} \rightleftharpoons N_{2\,(g)} + H_{2\,(g)}$$

In one of your experiments at 500 K the measured equilibrium partial pressures are:

Gas	Partial pressure (bar)
NH_3	0.887
H_2	0.168
N_2	0.0561

A. Determine the equilibrium constant for this reaction at 500 K. (6pt)

$$2\,NH_{3\,(g)} \rightleftharpoons N_{2\,(g)} + 3\,H_{2\,(g)} \qquad 2pt$$

$$K = \frac{P_{N_2}\,P_{H_2}^3}{P_{NH_3}^2} = \frac{(0.0561\,bar)(0.168\,bar)^3}{(0.887\,bar)^2} = 3.38 \times 10^{-4}$$

2pt   2pt   -1pt sig fig

B. You find in a publication that a researcher overseas has studied the same reaction at the same temperature, but she wrote the reaction in the form, $N_{2(g)} + H_{2(g)} \rightleftharpoons NH_{3(g)}$. Assuming you and the overseas researcher have done everything correctly, will her published value of K be the same as what you calculated in part a)? If they are not the same, what value of K do you expect to find in her publication?

(8pt)

No, not the same   2pt

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)} \qquad 2pt$$

$$K_{(b)} = \frac{1}{K_{(a)}} = \frac{P_{NH3}^2}{P_{N_2}\,P_{H_2}^3} = \frac{(0.887\,bar)^2}{(0.0561\,bar)(0.168\,bar)^3} = \frac{1}{3.38 \times 10^{-4}\,bar^2} = 2.96 \times 10^3$$

2pt   2pt   -1pt sig fig

During class there have been several excellent student questions.
All of the questions on this page are conceptual (no calculations required).

Q3

A. The conjugate acid of ¯OH is _____ (2pt)

H_2O

B. Which of the following produces the strongest conjugate base? _____ (4pt)

HF (pK_a = 3.45)   CH$_3$COOH (pK_a = 4.75)   HClO (pK_a = 7.53)

HIO (pK_a = 10.64)   HCOOH (pK_a = 3.75)

HIO (pK_a = 10.64)

C. For a 0.10 M solution of a weak acid, HA, with pK_a = 10,
which of the following is true? _____ (4pt)

[HA] ≅ 0   [HA] = K_a [HA] = [A¯]

[HA] ≠ [H$_3$O$^+$]   [HA] = [H$_3$O$^+$]

[HA] ≠ [H$_3$O$^+$]

D. Phosphoric acid (additive E338) is used to acidify foods and beverages such as various
colas and jams and provides a tangy or sour taste.
Write the reaction that represents K_{a_2} for phosphoric acid (H$_3$PO$_4$). (4pt)

$H_2PO_4^-$ (aq) + H_2O(l) ⇌ HPO_4^{2-} (aq) + H_3O^+(aq)
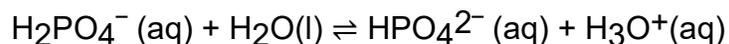
Q4. The main buffer in the blood consists primarily of hydrogen carbonate (HCO_3^-) and H_3O^+ ions in equilibrium with water and CO_2:

$$H_3O^+(aq) \ + \ HCO_3^- \ (aq) \ \rightleftharpoons \ 2\ H_2O(l) \ + \ CO_2(aq) \qquad K = 7.9 \times 10^{-7}$$
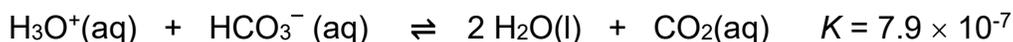
This reaction assumes that all H_2CO_3 produced decomposes completely to CO_2 and H_2O. Suppose that 1.0 L of blood is brought to pH = 6.1.

If the concentration of HCO_3^- is 5.5 µmol.L^{-1}, calculate the amount (in moles) of CO_2 present in the 1.0 L sample at pH = 6.1.   1 µmol.L^{-1} = 1 x 10^{-6} mol.L^{-1} (14 pt)

The pH is the solution at equilibrium. Use the equilibrium concentrations given.

"If the concentration of HCO_3^- is 5.5 µmol.L^{-1}, calculate the amount (in moles) of CO_2 present in the 1.0 L sample at pH = 6.1."

Using the pH to calculate [H_3O^+] and then describing it as the initial [H_3O^+] is a major misconception (-4pt). It results in the same answer if one approximates, we therefore gave 10pt (even with treating the equilibrium concentrations as the initial concentrations).
No ICE box is needed.

$$H_3O^+(aq) + HCO_3^- \rightleftharpoons 2\ H_2O(l) + CO_2(aq)$$
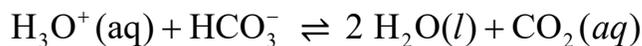
$$K = 7.9 \times 10^{-7} = \frac{[CO_2]}{[H_3O^+][HCO_3^-]}$$

Solving for $[CO_2]$:

$$[CO_2] = (7.9 \times 10^{-7})[H_3O^+][HCO_3^-]$$

Given: $[H_3O^+] = 10^{-6.1} = 7.9 \times 10^{-7}$ M, and $[HCO_3^-] = 5.5\ \mu\text{mol} \cdot L^{-1} = 5.5 \times 10^{-6}$ M

$$[CO_2] = (7.9 \times 10^{-7})(7.9 \times 10^{-7})(5.5 \times 10^{-6}) = 3.5 \times 10^{-18}\ \text{mol} \cdot L^{-1}$$

In 1.0 L of solution there will be 3.5×10^{-18} mol of CO_2 (aq)

2pt K expression

2pt rearranging to solve for [CO_2]

2pt calculating [H_3O^+]

2pt correct [HCO_3^-]

2pt correct [CO_2]

4pt final answer   -1pt units

Q5. Formic acid (also called methanoic acid) is the simplest carboxylic acid and is the main compound in ant venom. Formic acid, HCOOH, is what causes the 'burn' in ant bites. What is the pH of a 0.065 M solution of formic acid? (14pt)
Do not make approximations in your calculations.
HCOOH, $K_a = 1.80 \times 10^{-4}$

$$HCOOH(aq) \rightleftharpoons HCOO^-(aq) + H^+(aq) \qquad \text{3pt}$$

$K_a = [H^+][HCOO^-] / [HCOOH]$ 3pt

Let $[H+] = X$, then $[A-] = X$ and $[HA] = (0.065 - X)$

$1.80 \times 10^{-4} = X^2 / (0.065 - X)$

$1.17 \times 10^{-5} - 1.80 \times 10^{-4} X = X^2$

$X^2 + 1.80 \times 10^{-4} X - 1.17 \times 10^{-5} = 0$

$$X = \frac{-B +/- \sqrt{B^2 - 4AC}}{2A}$$

$X = 3.33 \times 10^{-3}$ 6pt

$pH = -\log[H+] = -\log 3.33 \times 10^{-3} = 2.48$ 2pt

In class, discussion sections, peer learning sessions, online discussion, office hours, review sessions, and study groups, thermochemistry and thermodynamics generated a lot of heat and work which added up to a lot of energy. ☺

Q6. After the winter quarter, you plan to enjoy a weekend BBQ during spring break using 4 moles of butane (C_4H_{10}) gas for cooking. What mass of butane will you need? Will this combustion reaction do expansion work? Calculate the change in internal energy for this reaction. Assume the reaction will occur at 1.00 atm and 300.°C, and the enthalpy of combustion of butane is -2878 kJ.mol^{-1}.   (14pt)

$$4\ CH_3CH_2CH_2CH_3(g)\ +\ 26\ O_2(g)\ \rightarrow\ 16\ CO_2(g)\ +\ 20\ H_2O(g)$$
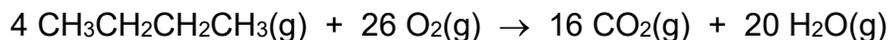
molar mass of butane = 58.12 g.mol^{-1} 2pt

mass butane needed = 4 mole x 58.12 g.mol^{-1} = 232.48 g   2pt

30 mol → 36 mol

Net number of moles of gas produced = 36 - 30 = 6 = Δn 2pt

Yes expansion work is done by this reaction.   2pt

ΔH = -2878 kJ.mol^{-1} x 4 mol = -11512 kJ   2pt

ΔU = q_p + w

ΔU = ΔH - PΔV 1pt

Use PV = nRT and PΔV = ΔnRT to obtain:

ΔU = ΔH - ΔnRT 1pt

0°C = 273.15 K

300.°C = 573.15 K

ΔU = -11512 kJ – 6 mol (8.314 J.K^{-1}.mol^{-1}) 573.15 K

ΔU = -11512 kJ – 28.591 kJ = -11,540.6 kJ = -11,541 kJ   2pt

-1pt units

Q7A. Determine the shift in equilibrium, if any, which will occur for the following reactions when the temperature is increased. Justify your answer. (8pt)

(i) Photosynthesis: $6\ CO_{2\ (g)} + 6\ H_2O_{\ (l)} \rightleftharpoons C_6H_{12}O_{6(s)} + 6\ O_{2\ (g)}$ $\Delta H_r° = +2802\ kJ.mol^{-1}$
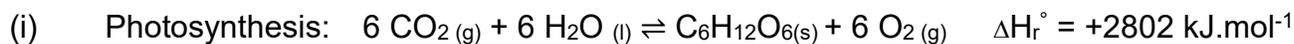
Equilibrium will shift right. 2pt
Since it is an endothermic reaction heating will favor product formation and K_C will increase. 2pt

(ii) ATP Hydrolysis: $ATP_{\ (aq)} + H_2O_{\ (l)} \rightleftharpoons ADP + PO_4^{2-}{}_{(aq)}$ $\Delta H_r° = -30\ kJ.mol^{-1}$
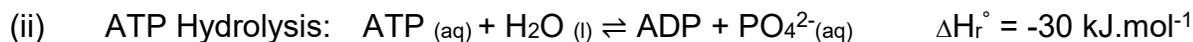
Equilibrium will shift left. 2pt
Since it is an exothermic reaction heating will favor reactant formation and K_C will decrease. 2pt

Q7B. A battery does 35 kJ of work driving an electric motor and 7 kJ of heat is released. What is the change in internal energy of the system? (4pt)

$\Delta U = q + w$ 2pt

$\Delta U = -7\ kJ - 35\ kJ = -42\ kJ$ 2pt -1pt units

Q7C. If an isolated system contained +5 kJ of energy, after 100 years U = ___+5 kJ___. (2pt)

Q7D. As discussed in class the burning of natural gas is a common energy source in power plants to generate electricity. Natural gas is a naturally occurring hydrocarbon gas mixture consisting primarily of methane, CH_4. Calculate the reaction enthalpy per mole of methane combustion using the data below. Is the reaction exothermic or endothermic? (8pt)

$\Delta H_B\ (O-H) = 463\ kJ.mol^{-1}$ $\Delta H_B\ (C-H) = 412\ kJ.mol^{-1}$
$\Delta H_B\ (C=O) = 743\ kJ.mol^{-1}$ $\Delta H_B\ (O_2) = 496\ kJ.mol^{-1}$

$CH_4\ +\ 2O_2\ \rightarrow\ CO_2\ +\ 2H_2O$ 2pt

$(4\ x\ 412)\ +\ (2\ x\ 496)$ $-\ (2\ x\ 743)\ -(4\ x\ 463)\ =\ -698\ kJ.mol^{-1}$ 4pt

exothermic 2pt -1 pt units

Chemistry Community has been super active this quarter with 10,172 online posts by week 5. Many student questions and great student-student discussion on the homework problems.

Q8A. Nanotechnologists have found ways to create and manipulate structures containing only a few molecules. However, orienting the molecules in specific ways to assemble such structures can be difficult. Calculate the entropy of a solid nanostructure made of 64 molecules in which the molecules (i) are all aligned in the same direction; (ii) lie in any one of four orientations with the same energy. (8pt)

(i)

$$W = 1^{64} = 1$$
$$S = k_B \ln W = k_B \ln 1 = 0$$

2pt

2pt

(ii)

$$S = k_B \ln W$$
$$W = 4^{64} = 3.403 \times 10^{38}$$
$$S = (1.3806 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(\ln(3.403 \times 10^{38}))$$
$$S = 1.22 \times 10^{-21} \text{ J} \cdot \text{K}^{-1}$$

2pt

2pt   -1pt units

Q8B. During the test of an internal combustion engine, 3.00 L of nitrogen gas (1.00 mol N_2 gas) at 18.5 °C was compressed suddenly (and irreversibly) to 0.500 L by driving in a piston. In the process the temperature of the gas increased to 28.1 °C. Assume ideal behavior. $N_2(g)$ $C_{V,m}$ = 20.81 J.K^{-1}.mol^{-1}. What is the change in entropy of the gas? (8pt)

Since entropy is a state function:
First calculate the decrease in entropy resulting from the decrease in volume (T constant).
Then calculate the increase in entropy resulting from the increase in temperature (V constant).
Then add these to get the net entropy change. See worked example in textbook.

$\Delta S = nR \ln\frac{V_2}{V_1}$ = (1.00 mol) (8.314 J·K^{-1}·mol^{-1}) ln (0.500 L/3.00 L)

= (1.00 mol) (8.314 J·K^{-1}·mol^{-1}) (-1.7917)
= -14.897 J·K^{-1}

T_1 = 18.5 + 273.15 = 291.65 K
T_2 = 28.1 + 273.15 = 301.25 K

$\Delta S = nC \ln\frac{T_2}{T_1}$ = (1.00 mol)(20.81 J.K^{-1}.mol^{-1}) ln (301.25 K/291.65 K)

= 0.674 J·K^{-1}

Net change in entropy, ΔS_{net} = (-14.897 + 0.674) J.K^{-1} = -14.2 J.K^{-1} 1pt each line   -1pt units

QXXX. In addition to discussion sections and Chemistry Community 24/7, the week before the midterm Dr. Lavelle organized a huge number of review sessions, peer learning sessions, and office hours. Were they helpful?   Yes/No _____