Second Semester Examination
2020/2021 Academic Session

July 2021

KFT332 – Physical Chemistry II

Duration: 2 hours

Please check that this examination paper consists of **EIGHT (8)** pages of printed material before you begin the examination.

Instructions:

This paper has **FIVE (5)** questions in **SECTIONS A** and **B**. Answer all **THREE (3)** questions from **SECTION A** and at least **ONE (1)** question from **SECTION B**.

Answer each question on a new page.

If a candidate answers more than four questions, only the answers to the first four questions in the answer sheet will be graded.

Appendix: Fundamental constants in physical chemistry.

SECTION A

1. (a) Determine ΔS if one mole of $N_2(g)$ is expanded from 20.0 L at 273 K to 300 L at 400 K. Assume that the molar heat capacity at constant pressure, $\bar{C}_P$, is 29.4 J K^{-1} mol^{-1} and is independent of temperature.

(5 marks)

(b) Show that

(i) $\Delta\bar{S} = \bar{C}_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$ for the change of one mole of an ideal gas from T_1, P_1 to T_2, P_2, assuming that $\bar{C}_P$ is independent of temperature.

(ii) dH = TdS + VdP starting from H(S, P).

(iii) $\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$ starting from H(T, P).

(15 marks)

(c) Starting from H = U + PV, prove that the Joule-Thomson coefficient can be written as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

(5 marks)

2. (a) Based on a graphical method, determine the partial molar volume of $ZnCl_2$ in 1 molal $ZnCl_2$ solution using the following data:

$[ZnCl_2]$/wt.%	2	6	10	14	18
Density/g cm^{-3}	1.0167	1.0532	1.0891	1.1275	1.1665

(8 marks)

(b) The vapour pressure of benzene (C_6H_6) and toluene (C_7H_8) have the following values in the temperature range between their boiling points at 1 bar:

T/°C	79.4	88	94	100	110
$P_{benzene}$/bar	1.000	1.285	1.526	1.801	-
$P_{toluene}$/bar	-	0.508	0.616	0.742	1.000

(i) Determine the compositions of the vapour and liquid phases at each temperature.

(ii) Sketch the boiling point diagram.

(iii) If a solution containing 0.5 mole fraction of benzene and 0.5 mole fraction of toluene is heated to a specific temperature, the first vapour bubble will appear. Determine the temperature when the first vapour bubble appears and composition of the vapour.

(12 marks)

(c) A container has a double wall where the wall cavity is filled with CO_2 at 298 K and 1 atm. When the container is filled with liquid nitrogen at 100 K, the CO_2 will freeze so that the wall cavity has a mixture of solid and vapour CO_2 at sublimation pressure. Assume that the data for CO_2 at 100 K is not available, but it is known that the sublimation pressure, $P_{sublimation}$, and enthalpy of sublimation, $\Delta H_{sublimation}$, for CO_2 at -90 °C are 38.1 kPa and 574.5 kJ kg^{-1}, respectively. Determine the pressure in the wall cavity at 100 K.

(5 marks)

3. (a) The following emf values, E, were obtained at 25 °C for the cell at various molalities, m, of LiCl:

$$\text{Pt, } H_2(1 \text{ bar}) \mid \text{LiOH}(0.01\text{m}), \text{LiCl(m)} \mid \text{AgCl(s)} \mid \text{Ag}$$

m/mol kg^{-1}	0.01	0.02	0.05	0.10	0.20
E/V	1.0498	1.0318	1.0076	0.9888	0.9696

Given that $E^{o}_{AgCl/Ag}$= 0.2224 V, calculate the ionic product of water, K_w.

(15 marks)

(b) In the Debye-Hückel limiting law, the relationship between the activity coefficient, $\gamma_{\pm}$, and the ionic strength, I, of a dilute solution is

$$-\ln\gamma_{\pm} = |Z_{+}Z_{-}|A\sqrt{I}$$

where Z_+ and Z_- are the charges on the positive and negative ions, respectively. The constant A is given by the expression

$$A \ (\text{in unit of in molal}^{-1/2}) \ = \sqrt{(2\pi N_A \rho_{sol})\left(\frac{e^2}{4\pi\varepsilon_o\varepsilon_r kT}\right)}$$

where N_A = Avogadro number, $\rho_{solvent}$ = density of solvent (in unit of kg m^{-3}), e = charge in C, ε_o = permittivity of free space, ε_r = dielectric constant of solvent, k = Boltzmann's constant and T = absolute temperature in K.

(i) Determine the A value in water at 25 °C.
Given ρ_{water} = 997 kg m^{-3} at 25 °C, ε_o = 8.854 ×10^{-12} C^2 J^{-1} m^{-1} and ε_r = 78.54.

(ii) From (i), calculate the ionic strength, I, if the mean activity coefficients, $\gamma_{\pm}$, for HCl and $CaCl_2$ are 0.964 and 0.880, respectively, using the Debye-Hückel limiting law.

(10 marks)

SECTION B

4. (a) The table below shows the values for the molar solubility, s, of thallium iodate, $TlIO_3$, in solutions of potassium chloride, KCl, at 298 K:

m (KCl)/mol kg^{-1}	0.005	0.01	0.02	0.05
s ($TlIO_3$)/mol kg^{-1}	0.00193	0.00200	0.00210	0.00232

Assuming that the dissociation of both salts was complete, calculate

(i) the solubility product, K_{sp}, of the $TlIO_3$.

(ii) the mean ionic activity coefficient, $\gamma_{\pm}$, for $TlIO_3$ in solution of 0.02 mol kg^{-1} KCl.

(iii) the A value using the Debye-Hückel limiting law.

(iv) the solubility, s, of $TlIO_3$ in water.

(10 marks)

(b) Ethanol and methanol form very nearly ideal solutions. At 20 °C, the vapour pressure of ethanol and methanol are 5.93 kPa and 11.83 kPa, respectively. Calculate

(i) the mole fractions of methanol and ethanol in a solution obtained by mixing 100 g of each.

(ii) the partial pressures and total vapour pressure of the solution.

(iii) the mole fraction of methanol in the vapour.

(7 marks)

(c) Consider the following reaction and thermodynamic data:

$$CO(NH_2)_2(aq) + H_2O(\ell) \rightarrow CO_2(g) + 2NH_3(g)$$

Substance	$\Delta_f H°$/kJ mol^{-1}	$S°$/J K^{-1} mol^{-1}
$CO(NH_2)_2(aq)$	-391.2	173.8
$H_2O(\ell)$	-285.9	69.96
$CO_2(g)$	-393.5	213.6
$NH_3(g)$	-46.19	192.5

(i) Calculate the change in standard Gibbs free energy, $\Delta G°$, for this reaction at 25 °C.

(ii) Determine the minimum temperature for the reaction to be spontaneous.

(8 marks)

5. (a) A reasonable approximation to the vapour phase of krypton is given by

$$\mathrm{Log}_{10}(\mathrm{P/Torr}) = \mathrm{b} - 0.05223(\frac{\mathrm{a}}{\mathrm{T}})$$

For solid krypton, a = 10065 K and b = 7.1770. For liquid krypton, a = 9377 K and b = 6.92387. Using this information, deduce

(i) the triple point temperature and pressure.

(ii) the $\Delta H_{vaporisation}$, ΔH_{fusion} and $\Delta H_{sublimation}$ of krypton.

(10 marks)

(b) Air is a mixture of gases with the following mass percentage composition: 75.52% N_2, 23.15% O_2, 1.28% Ar and 0.046% CO_2.

(i) Determine the partial pressure of N_2, O_2, Ar and CO_2 when the total pressure is 1.100 atm.

(ii) Calculate the molar entropy of mixing, Δs_{mix}, for air at 1.100 atm and 25 °C in a 10-L container, assuming ideal-gas behaviour is obeyed.

(7 marks)

(c) Consider the following cell:

$$\mathrm{Pt}\,|\,\mathrm{Fe}\,|\,\mathrm{Fe^{2+}}\,|\,\mathrm{Fe^{2+}},\ \mathrm{Fe^{3+}}\,|\,\mathrm{Pt}$$

The temperature coefficient of emf, $\left(\frac{\delta E}{\delta T}\right)_P$, for the cell is 1.14 mV K^{-1} at 273.15 K. Calculate

(i) the change in entropy, ΔS^o.

(ii) the change in Gibbs free energy, ΔG^o.

(iii) the change in enthalpy, ΔH^o.

Given that $E^o_{Fe^{3+}/Fe^{2+}} = 0.771\ V$ and $E^o_{Fe^{2+}/Fe} = -0.447\ V$.

(8 marks)

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General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.99792458	10^{8}	$m\ s^{-1}$
Elementary charge	e	1.60218	10^{-19}	C
Faraday constant	$F = N_Ae$	9.64853	10^{4}	$C\ mol^{-1}$
Boltzmann constant	k	1.38065	10^{-23}	$J\ K^{-1}$
Mass of electron	m_e	9.10938356	10^{-31}	kg
Gas constant	$R = N_Ak$	8.31447		$J\ K^{-1}\ mol^{-1}$
		8.31447	10^{-2}	$L\ bar\ K^{-1}\ mol^{-1}$
		8.20574	10^{-2}	$L\ atm\ K^{-1}\ mol^{-1}$
		6.23637	10	$LTorr\ K^{-1}\ mol^{-1}$
Planck constant	h	6.62608	10^{-34}	J s
	$\hbar = h/2\pi$	1.05457	10^{-34}	J s
Avogadro constant	N_A	6.02214	10^{23}	mol^{-1}
Standard acceleration of free fall	g	9.80665		$m\ s^{-2}$

Conversion factors		Useful relation	Unit relations	
1 eV	1.60218×10^{-19} J 96.485 kJ mol^{-1} 8065.5 cm^{-1}	2.303 RT/F = 0.0591 V at 25 °C	Energy	1 J = 1 kg $m^2\ s^{-2}$ = 1 A V s
			Force	1 N = 1 kg m s^{-2}
1 cal	4.184 J		Pressure	1 Pa = 1 N m^{-2} = 1 kg $m^{-1}\ s^{-2}$ = 1 J m^{-3}
1 atm	1.013 bar 101.325 kPa 760 Torr			
1 cm^{-1}	1.9864×10^{-23} J		Charge	1 C = 1 A s
1 Å 1 L atm	10^{-10} m 101.325 J		Potential difference	1 V = 1 J C^{-1} = 1 kg $m^2\ s^{-3}\ A^{-1}$

Atomic weights

Al	26.98	C	12.01	Fe	55.85	P	30.97
Sb	121.76	Cs	132.92	Kr	83.80	K	39.098
Ar	39.95	Cl	35.45	Pb	207.2	Ag	107.87
As	74.92	Cr	51.996	Li	6.941	Na	22.99
Ba	137.33	Co	58.93	Mg	24.31	S	32.066
Be	9.012	Cu	63.55	Mn	54.94	Sn	118.71
Bi	208.98	F	18.998	Hg	200.59	W	183.84
B	10.81	Au	196.97	Ne	20.18	Xe	131.29
Br	79.90	He	4.002	Ni	58.69	Zn	65.39
Cd	112.41	H	1.008	N	14.01		
Ca	40.078	I	126.90	O	15.999		

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