EXAM 3
November 11, 2013

IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give some reasoning or working for each answer. Full marks will NOT be awarded for the final answer by itself, UNLESS it is supported by a brief justification or explanation.
Give units for all quantities!

YOUR NAME   SOLUTIONS

Some data: $R = 8.314$ J K^{-1} mol^{-1} $N_A = 6.022 \times 10^{23}$ mol^{-1} 1 atm = 101325 Pa

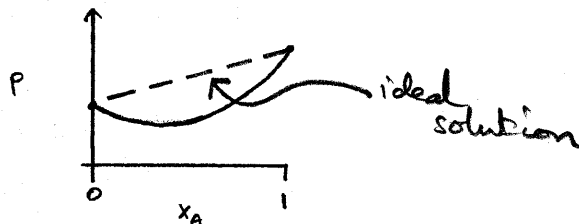$$dU = dq + dw \qquad dS = dq_{rev}/T \qquad \gamma = C_p/C_V \qquad C_p - C_V = nR$$

$$dw = -p_{ex}\, dV \qquad \text{Heat engine } \varepsilon = (T_h - T_c)/T_h \qquad \text{adiabat: } pV^{\gamma} = const$$

$$H = U + pV \qquad G = H - TS \qquad A = U - TS$$

$$d \ln K / d\,(1/T) = -\Delta H/R \qquad \Delta_r G = \Delta G^{\circ} + RT \ln Q$$

(1)   *30 points*

i)   Here is a plot of vapor pressure as function of composition for a mixture of two liquids A and B. Is the deviation from Raoult's Law positive or negative? Interpret this deviation in terms of intermolecular forces in the system.

ii)   Starting from the Clausius equation $dp/dT = \Delta S/\Delta V$ for a phase transition, deduce the approximate Clausius-Clapeyron relation $dp/dT = p\,\Delta_{vap}H/(RT^2)$ for a liquid to gas transition. *Show work.*

i) Because the pressure is lower than for an ideal solution, this is a negative deviation.
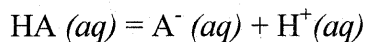The average A-B forces are stronger (more attractive) than A-A and B-B.

ii) $\Delta S = \dfrac{\Delta_{vap}H}{T}$ for reversible vaporization

$\Delta V = V_{gas} - V_{liquid} \approx V_{gas} = \dfrac{RT}{P}$ for 1 mol

$\therefore \dfrac{dp}{dT} = \dfrac{\Delta_{vap}H}{T} \div \dfrac{RT}{P} = \dfrac{P\,\Delta_{vap}H}{RT^2}$

(2)   *30 points*

Trichloroacetic acid "HA" dissociates in water. Writing A for $C(O)CCl_3$,
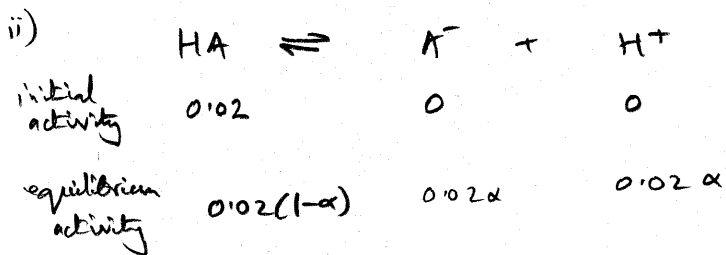
$$HA\ (aq) = A^-\ (aq) + H^+(aq)$$

Assume the solutions are ideal and at 298 K.

i)   Estimate the pH of an initially 0.02 M solution of HA if it all dissociates.

ii)   Find the degree of dissociation α of HA in an initially 0.02 M solution of HA, and the pH at equilibrium, if the equilibrium constant K_a is 0.2. Do not assume α is small.

iii) Calculate the reaction Gibbs function when [HA] = 0.003 M, [H^+] = 0.01 M and [A^-] = 0.2 M. What is the corresponding direction of spontaneous reaction? *Show work and justify your answer.*

i) If HA dissociates completely then [H^+] will be 0.02 M.

$a_{H^+} = 0.02M/1M = 0.02$, $pH = -\log_{10} a_{H^+} = \underline{1.70}$.

ii)

$$HA \rightleftharpoons A^- + H^+$$

initial activity   0.02   0   0

equilibrium activity   0.02(1-α)   0.02α 0.02α

$$K_a = \frac{0.02^2 \alpha^2}{0.02(1-\alpha)} = \frac{0.02\,\alpha^2}{1-\alpha} = 0.2$$

$\therefore\ 0.02\alpha^2 = 0.2 - 0.2\alpha\ \therefore\ 0.02\alpha^2 + 0.2\alpha - 0.2 = 0$

$\therefore\ 0.1\alpha^2 + \alpha - 1 = 0$

$\therefore\ \alpha = \dfrac{-1 \pm \sqrt{1^2 - 4\times0.1\times-1}}{0.2} = \dfrac{-1 \pm \sqrt{1.4}}{0.2}$ α must be positive

$= 0.183/0.2 = \underline{0.916}$.

$a_{H^+} = 0.02\alpha = 0.0183\ \therefore pH = \underline{1.74}$.

iii) $\Delta_r G = \Delta G^\ominus + RT \ln Q$ $Q = \dfrac{0.2 \times 0.01}{0.003} = 0.667$

$= -RT\ln K + RT\ln Q$

$= 3987 - 1004\ J\,mol^{-1}$

$= 2983\ J\,mol^{-1}$

$> 0\ \therefore$ spontaneous direction is to make more HA, i.e., R to L.
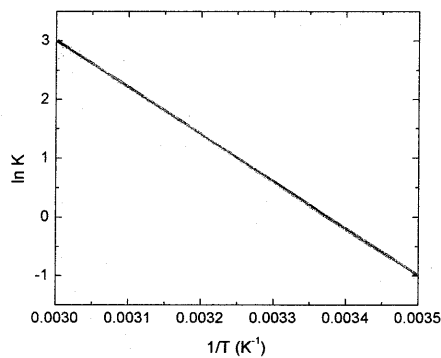

Page 3

(3)   *40 points*

i)   Starting from ΔG in terms of ln K, the Gibbs-Helmholtz equation,

$$\frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

and the assumption that ΔH is independent of temperature, prove that d ln K/d (1/T) = $-\Delta H/R$.

ii)   From this graph, estimate ΔH and ΔS.

i) $\Delta G = -RT \ln K$

$\therefore \frac{\Delta G}{T} = -R \ln K$

$\frac{d \, \Delta G/T}{dT} = -R \frac{d \ln K}{dT} = -\frac{\Delta H}{T^2}$ $\therefore \frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$.

$\frac{d \ln K}{d \, 1/T} = \frac{d \ln K}{dT} \cdot \frac{dT}{d \, 1/T} = \frac{\Delta H}{RT^2} \cdot -T^2 = -\frac{\Delta H}{R}$. $\left(\frac{d}{dT} T^{-1} = \frac{-1}{T^2} \right)$

ii) slope $= \frac{3-(-1)}{0.0030 - 0.0035 \ K^{-1}} = -8000 K$

$\therefore \Delta H = -R \times 8000 \ K = +66512 \ J \ mol^{-1} = +66.5 \ kJ \ mol^{-1}$.

When $1/T = 0.0030 \ K^{-1}$, $\ln K = 3$ $\therefore \Delta G = -RT \ln K$

$= -R \left(\frac{1}{0.0030 \ K^{-1}} \right) \cdot 3$

$= -8314 \ J \ mol^{-1} \ or \ -8.3 \ kJ \ mol^{-1}$.

$= \Delta H - T \Delta S$

$\therefore \Delta S = \frac{\Delta G - \Delta H}{T} = \frac{-8314 - 66512 \ J \ mol^{-1}}{-333 \ K} = +225 \ J \ mol^{-1} K^{-1}$.