IMPORTANT: Write clearly and neatly. 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} 1 atm $= 101325$ Pa $N_A = 6.022 \times 10^{23}$ mol^{-1} $\gamma = C_p/C_v$

$C_p - C_v = nR$ $dU = dq + dw$ $dS = dq/T$ $H = U + pV$ $G = H - TS$ $A = U - TS$

Trouton's constant $= 85$ J K^{-1} mol^{-1}

(1)   30 points

An equilibrium constant K is found to obey

$$\ln K = -4.7 - 1200/T - 0.3\,T$$

where T is in kelvin. Calculate ΔH, then ΔG, then ΔS, all at 298 K. Give units.

$$\frac{d\ln K}{d\,1/T} = -1200 - 0.3\,\frac{1}{(d\,1/T/dT)} = -1200 + 0.3\,T^2 = -\frac{\Delta H}{R}$$

$$= 25441 \text{ at } 298\,K$$

$$\therefore \Delta H = -211.5 \text{ kJ mol}^{-1},$$

At 298 K, $\ln K = -4.7 - 4.027 - 89.4 = -98.13$

$$\therefore \Delta G = -RT \ln K = +243.1 \text{ kJ mol}^{-1}$$

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

$$\therefore \Delta S = \frac{\Delta H - \Delta G}{T} = -1526 \text{ J K}^{-1} \text{ mol}^{-1},$$

(2)   *30 points*

Consider the dissociation of hydrocyanic acid in aqueous solution $HCN \rightarrow CN^- + H^+$

for which K_a is 4.9×10^{-10}.

(i) Find the pH of a solution initially 10^{-2} M in HCN, and the degree of dissociation of the HCN, α.

(ii) To this solution is added more CN^- until $[CN^-] = 0.1$ M. What is the new pH of the solution?

(iii) Without making a new numerical calculation, explain qualitatively how the degree of dissociation would change if the solution is diluted.

i)

$$HCN \rightleftharpoons H^+ + CN^-$$
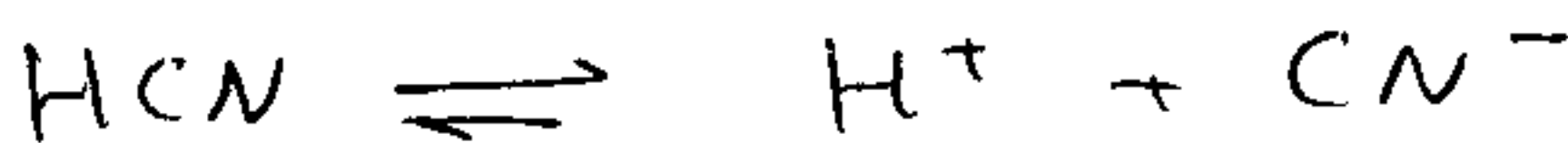
initial activity   0.01   0   0
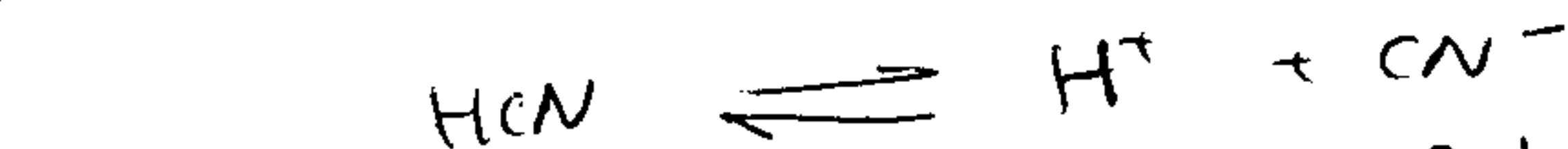
final activity   0.01-x   x   x

$$\frac{x^2}{0.01-x} = K_a = 4.9 \times 10^{-10} \quad \therefore \quad x^2 + 4.9 \times 10^{-10} x - 4.9 \times 10^{-12} = 0$$

$$\therefore \quad x = \frac{-4.9 \times 10^{-10} \pm \sqrt{(4.9 \times 10^{-10})^2 + 4 \times 4.9 \times 10^{-12}}}{2}$$

The positive root is 2.21×10^{-6}. The pH $= -\log_{10} x = \underline{\underline{5.66}}$.

$$\alpha = \frac{x}{0.01} = \underline{\underline{2.21 \times 10^{-4}}}.$$

ii) x is so small that the initial [HCN] is still about 0.01 M.

$$HCN \rightleftharpoons H^+ + CN^-$$

initial activity   0.01   ≈0   0.1

final activity   0.01   x   0.1

(because $x \ll 0.01$, [HCN] and [CN$^-$] are almost constant)

$$\frac{0.1 \, x}{0.01} = K_a \quad \therefore \quad x \approx 4.9 \times 10^{-11} \text{ and the pH} = \underline{\underline{+10.31}}.$$

iii) By Le Chatelier's principle, dilution increases α.

(3)   *40 points*

i)   Starting with an expression for the differential of G, derive the Maxwell relation for $(\partial V/\partial T)_p$
Points will be awarded for a demonstrated understanding so it is critical to explain each step.
Example:

STEP	EXPLANATION
whatever mathematical step	commonly known formula
whatever mathematical step	integrated
whatever mathematical step	because of such-and-such property, X = Y
etc.	

ii)   Use this result to find ΔS for the isothermal expansion of 1 mol of a real gas from a pressure p_1 to p_2, where the equation of state is $p^x V = RT$ where x is a constant ($x \neq 1$).

i) $dU = dq + dw = TdS - pdV$.

$dH = dU + d(pV) = TdS - pdV + pdV + Vdp$

$dG = dH - d(TS) = TdS + Vdp - TdS - SdT$

$= Vdp - SdT$.

Consider $G(p,T)$ so $dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$.

By comparing terms $V = \left(\frac{\partial G}{\partial p}\right)_T$ and $-S = \left(\frac{\partial G}{\partial T}\right)_p$.

The order of differentiation for a second derivative does not matter,

thus $\frac{\partial^2 G}{\partial p \partial T} = \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$.

ii) $\Delta S = \int dS = \int \left(\frac{\partial S}{\partial p}\right)_T \cdot dp$ for an isothermal process.

Here, $V = RTp^{-x}$ $\therefore \left(\frac{\partial V}{\partial T}\right)_p = Rp^{-x}$

$\therefore \Delta S = \int_{p_1}^{p_2} -R \cdot p^{-x} dp = \frac{R}{x-1}\left(p_2^{1-x} - p_1^{1-x}\right)$.