

## EXAM 4

November 21, 2018

*IMPORTANT: Write neatly and lay out solutions clearly. Make sure that you give 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:  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$   $1 \text{ atm} = 101325 \text{ Pa}$

$$dU = dq + dw \quad dS = dq_{\text{rev}}/T \quad \gamma = C_p/C_v \quad C_p - C_v = nR$$

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

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

$$k = A \exp(-E_a/(RT)) \quad \text{mean K.E.} = 1.5 k_B T$$

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

(1) 30 points

Consider the reaction  $A \rightarrow B$  which has the rate law  $v = k [A]^{2.5}$ . Initially  $[A] = a_0$ .

Derive an expression for  $[A]$  as a function of time and use this result to determine the half-life of A. Show work. Give an example of appropriate units for k.

$$v = -\frac{d[A]}{dt} = k [A]^{2.5}$$

$$\therefore \int \frac{-d[A]}{[A]^{2.5}} = \int k dt$$

$$\therefore \frac{2}{3} [A]^{-1.5} = kt + c$$

$$\text{when } t=0, [A]=a_0 \therefore c = \frac{2}{3} a_0^{-1.5}$$

$$\frac{2}{3} [A]^{-1.5} - \frac{2}{3} a_0^{-1.5} = kt$$

$$\text{when } t = t_{1/2}, [A] = a_0/2 \text{ so}$$

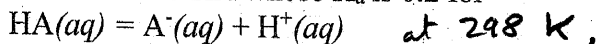
$$\frac{2}{3} [a_0/2]^{-1.5} - \frac{2}{3} a_0^{-1.5} = kt_{1/2}$$

$$\therefore t_{1/2} = \frac{1}{k} \frac{2}{3} a_0^{-1.5} (2^{1.5} - 1)$$

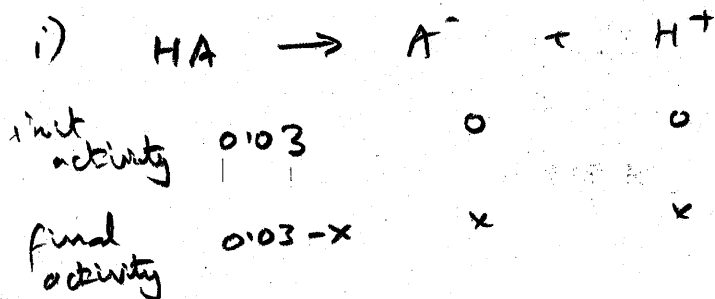
k could have units of  $M^{-1.5} s^{-1}$ .

(2) 30 points

Consider a weak acid HA whose  $K_a$  is 0.2 for



- i) Consider a solution of HA with an initial concentration of  $0.03 \text{ mol dm}^{-3}$  which comes to equilibrium. Find the degree of dissociation  $\alpha$  of HA and the pH. Do not assume  $\alpha$  is small.
- ii) When  $[\text{HA}] = 2 \times 10^{-8} \text{ M}$ ,  $[\text{A}^-] = 3 \times 10^{-5} \text{ M}$  and  $[\text{H}^+] = 5 \times 10^{-5} \text{ M}$ , what is the value of the reaction Gibbs function and what direction of spontaneous reaction is therefore predicted?



$$0.2 = K_a = \frac{x^2}{0.03-x} \quad \therefore x^2 = -0.2x + 0.006$$
$$\therefore x^2 + 0.2x - 0.006 = 0$$

$$\therefore x = \frac{-0.2 \pm \sqrt{0.2^2 + 4 \times 0.006}}{2} = \frac{-0.2 \pm 0.253}{2}$$

$x$  must be positive so  $x = 0.0265$

$$\text{pH} = -\log_{10} x = \underline{\underline{1.58}}$$

In terms of  $\alpha$ ,  $0.03 - x = 0.03(1 - \alpha)$   
 $= 0.03 - 0.03\alpha$

$$\therefore \alpha = \frac{x}{0.03} = \underline{\underline{0.88}}$$

$$\text{ii)} \quad Q = \frac{3 \times 10^{-5} \times 5 \times 10^{-5}}{2 \times 10^{-8}} = 0.075 \quad \therefore RT \ln Q = -6418 \text{ J mol}^{-1}$$

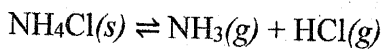
$$\Delta G^\circ = -RT \ln K = 3987 \text{ J mol}^{-1}$$

$$\Delta_r G = \Delta G^\circ + RT \ln Q = -2431 \text{ J mol}^{-1} < 0$$

$\therefore$  spontaneous in forward direction.

(3) 40 points

When  $\text{NH}_4\text{Cl}(s)$  is heated it dissociates to  $\text{NH}_3(g)$  and  $\text{HCl}(g)$ . Consider the equilibrium



and the information that at 700 K the total gas pressure is  $6.0 \times 10^5$  Pa, increasing to  $1.8 \times 10^6$  Pa at 750 K. Deduce  $\Delta G^\circ$  at 700 K. Find  $\Delta H^\circ$  and  $\Delta S^\circ$  for this reaction, assuming they do not vary with temperature.

Because  $p = p_{\text{NH}_3} + p_{\text{HCl}}$  and these are equal,

$$p_{\text{NH}_3} = p_{\text{HCl}} = \frac{1}{2} p.$$

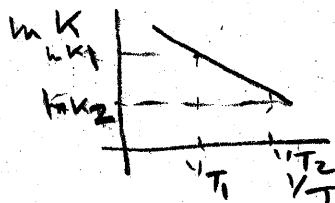
$$K = \frac{a_{\text{NH}_3} \cdot a_{\text{HCl}}}{a_{\text{NH}_4\text{Cl}}} \quad \text{and} \quad a_{\text{NH}_4\text{Cl}} = 1$$

$$\therefore K = \frac{1}{2} (p/p^\circ) \times \frac{1}{2} (p/p^\circ) =$$

$$K_{700} = \left(\frac{1}{2} \times 6\right)^2 = 9.$$

$$\Delta G^\circ = -RT \ln K = -12787 \text{ J mol}^{-1} \text{ at } 700 \text{ K.}$$

$$K_{750} = \left(\frac{1}{2} \times 18\right)^2 = 81.$$



$$\text{slope} = -\frac{\Delta H}{R} = \ln(K_2/K_1) \div \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= \ln(81/9) \div \left(\frac{1}{750} - \frac{1}{700}\right)$$

$$= 2.197 \div -9.52 \times 10^{-5} = -2.31 \times 10^4$$

$$\therefore \Delta H = +1.92 \times 10^5 \text{ J mol}^{-1} = +192 \text{ kJ mol}^{-1}.$$

$$\text{At } 700 \text{ K, } \Delta G = \Delta H - T\Delta S$$

$$\therefore \Delta S = \frac{\Delta H - \Delta G}{T} = \frac{1.92 \times 10^5 + 12787}{700} \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 292 \text{ J mol}^{-1} \text{ K}^{-1}.$$

see homework ex 6 B7.