PHYSICAL CHEMISTRY 5200

QUIZ 2

November 21, 2019

Please write neatly and clearly, and <u>show all working</u>. Allocate time to each question in proportion to the available credit. Keep any explanations brief and to the point.

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

N_A or $L = 6.022 \times 10^{23}$ mol^{-1} $R = 8.314$ J K^{-1} mol^{-1}

k or $k_B = R/N_A$

$dU = dq + dw$ $H = U + pV$

$dw = -p_{ex}\, dV$ $\gamma = C_p/C_v$

Perfect gas: $pV = nRT$ and $C_p - C_v = nR$

van der Waals gas: $p = nRT/(V-b) - a(n/V)^2$

Adiabat: pV^γ is constant   Heat engine $\varepsilon = (T_h - T_c)/T_h$

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

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

$pH = -\log_{10}(a_{H+})$ $k = A \exp(-E_a/RT)$
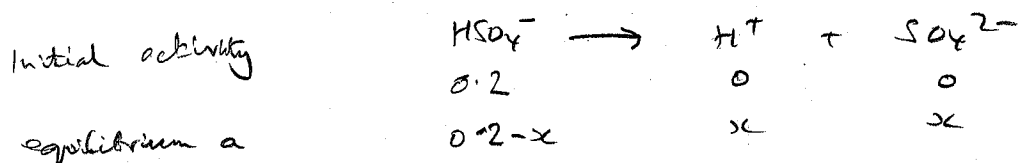
1) **25 points**

Consider the reaction HSO_4^- *(aq)* $\rightleftharpoons H^+$ *(aq)* $+ SO_4^{2-}$ *(aq)* for which ΔG^0 at 298 K is +11.0 kJ mol^{-1} and $\Delta H^0 = +25.1$ kJ mol^{-1}.

a) What is the pH of an initially 0.2 M solution of HSO_4^- at 298 K? What is the degree of dissociation α of HSO_4^- here?

b) Explain what Le Chatelier's principle predicts will be the trend for α if the temperature is lowered?

c) Calculate the pH of an initially 0.2 M solution of HSO_4^- at 273 K.

a) $K = e^{-\Delta G/RT} = e^{-11000/(8.314 \times 298)} = 0.0118.$

Initial activity

$$HSO_4^- \longrightarrow H^+ + SO_4^{2-}$$

$$0.2 \qquad\qquad 0 \qquad 0$$

equilibrium a

$$0.2-x \qquad\qquad x \qquad x$$

$$\frac{x^2}{0.2-x} = K \therefore x^2 = 0.2K - Kx \therefore x^2 + Kx - 0.2K = 0$$

$$x = \frac{-0.0118 \pm \sqrt{0.0118^2 + 0.8 \times 0.0118}}{2}$$

$$= \frac{-0.0118 \pm 0.0979}{2} = 0.0430 \text{ or } -0.0549 \text{ unreasonable}$$

$$pH = -\log_{10}(0.0430) = 1.37.$$

$$\alpha = x/0.2 = 0.215,$$

b) System moves in direction that releases heat i.e. to the left, smaller α.

c) $\Delta G = \Delta H - T\Delta S$ so $\Delta S = \frac{\Delta H - \Delta G}{T} = 47.3$ $JK^{-1}mol^{-1}$ using 298K data.

ΔG at 273 $= \Delta H - T\Delta S = 12187$ $Jmol^{-1} \therefore K = 0.00466$

$$x = \frac{-0.00466 \pm \sqrt{0.00375}}{2} = 0.0283$$

$$\therefore pH = -\log_{10}(0.0283) = 1.55.$$

Or you could use $\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \therefore \ln\left(\frac{K_2}{K_1}\right) = -3019\left(\frac{1}{273} - \frac{1}{298}\right)$

$$= -0.927$$

$$\therefore K_2/K_1 = 0.395 \therefore K_2 = 0.395 \times 0.0118 = 0.00466.$$

2)   25 *points*

The reaction A → Z is found to be third-order in A.

a) What are consistent units for the rate constant k?

b) Assuming one starts with pure A at a concentration $[A]_0$, deduce the integrated rate law for [A] as a function of time. What plot of measured [A], t data would give a straight line?

c) [A] is found to drop from 0.3 M to 0.15 M in 20 seconds. What is the value of k?

d) If raising the temperature from 298 to 310 K increases the rate constant by a factor of 2.0, what is the activation energy E_a?

a) $v = -\dfrac{d[A]}{dt} = k[A]^3$ so units of k are $M s^{-1} \div M^3 = M^{-2} s^{-1}$.

b)

$$\dfrac{d[A]}{[A]^3} = -k\,dt \quad \therefore \quad \int_{[A]_0}^{[A]} [A]^{-3} dA = -k\int_0^t dt = -kt$$

$$\therefore \left[-\tfrac{1}{2}[A]^{-2}\right]_{[A]_0}^{[A]} = -kt = \tfrac{1}{2}\left\{\dfrac{1}{[A]^2} - \dfrac{1}{[A]_0^2}\right\}$$

$$\therefore \quad 2kt = \dfrac{1}{[A]^2} - \dfrac{1}{[A]_0^2} \quad \text{so} \quad \dfrac{1}{[A]^2} = \dfrac{1}{[A]_0^2} + 2kt$$

Plot $\dfrac{1}{[A]^2}$ vs t, slope is $2k$.

c) Half life is 20s.

$$\dfrac{1}{([A]_0/2)^2} = \dfrac{1}{[A]_0^2} + 2kt_{1/2}$$

$$\therefore \quad 2kt_{1/2} = \dfrac{4}{[A]_0^2} - \dfrac{1}{[A]_0^2} = \dfrac{3}{[A]_0^2} \quad \therefore \quad t_{1/2} = \dfrac{3}{2}\dfrac{1}{k}\dfrac{1}{[A]_0^2}$$

$$= \dfrac{16.7\, M^{-2}}{k} \text{ here}$$

So $k = \dfrac{16.7\, M^{-2}}{20\, s} = 0.833\ M^{-2} s^{-1}$.

d) $\ln k = A - \dfrac{E_a}{RT}$

so $\ln\left(\dfrac{k_1}{k_2}\right) = -\dfrac{E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$\therefore \ln 2 = -\dfrac{E_a}{R}\left(\dfrac{1}{310} - \dfrac{1}{298}\right)$

$\therefore -\dfrac{E_a}{R} = -5336\ K \quad \therefore \quad E_a = 44.4\ kJ\ mol^{-1}$.