

## EXAM 4

28 November 2012

*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 possibly useful information:

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

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

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

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

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

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

(1) 40 points

Consider formic acid HCOOH dissolving in water:

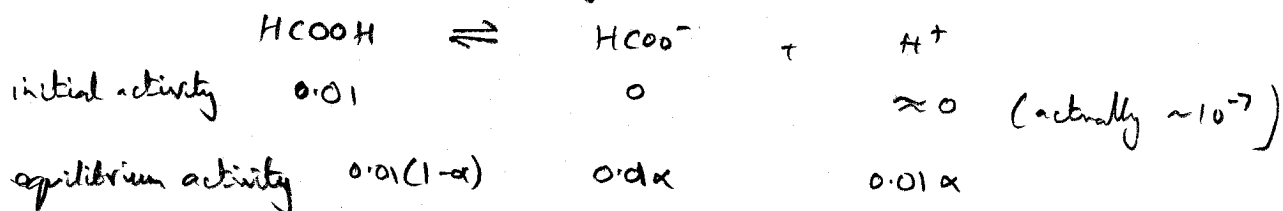


with equilibrium constant  $K_a = 3 \times 10^{-3}$  at 298 K. Assume the solution is ideal.

a) Find the degree of dissociation  $\alpha$  for an initially 0.01 M solution of HCOOH. What is the pH at equilibrium?

b)  $K_a$  is  $1 \times 10^{-2}$  at 320 K. Deduce  $\Delta H$  for the dissociation reaction.

i) For an ideal solution, activity  $a = \text{concentration} \div 1 \text{ M}$ .



$$K_a = \frac{(0.01\alpha)^2}{0.01(1-\alpha)} = \frac{0.01\alpha^2}{1-\alpha} = 0.003 \quad \therefore \frac{\alpha^2}{1-\alpha} = 0.3 \quad \therefore \alpha^2 + 0.3\alpha - 0.3 = 0$$

$$\text{Quadratic formula } \alpha = \frac{-0.3 \pm \sqrt{0.3^2 + 4 \times 0.3}}{2} = \frac{-0.3 \pm \sqrt{1.29}}{2} = \underline{\underline{0.418}} \quad (\text{the negative solution is impossible})$$

$$a_{\text{H}^+} = 0.01\alpha = 0.00418 \quad \text{pH} = -\log_{10}(a_{\text{H}^+}) = -\log_{10} 0.00418 = \underline{\underline{2.38}}$$

b) Slope of a van't Hoff plot =  $\frac{d \ln K}{d 1/T} = \frac{-\Delta H}{R}$

$$\Delta \ln K = \ln 3 \times 10^{-3} - \ln 1 \times 10^{-2} = -5.809 + 4.605 = -1.204$$

$$\Delta 1/T = \frac{1}{298 \text{ K}} - \frac{1}{310 \text{ K}} = 2.307 \times 10^{-4} \text{ K}^{-1}$$

$$\frac{-\Delta H}{R} = \frac{-1.204}{2.307 \times 10^{-4} \text{ K}^{-1}} = -5.219 \times 10^3 \text{ K}$$

$$\begin{aligned} \therefore \Delta H &= 5.219 \text{ J mol}^{-1} \text{ K}^{-1} \times +5.219 \times 10^3 \text{ K} \\ &= 4.339 \times 10^4 \text{ J mol}^{-1} \\ &= \underline{\underline{43.39 \text{ kJ mol}^{-1}}} \end{aligned}$$

(2) 40 points

Imagine the reaction  $A \rightarrow 2B$  with a rate law  $v = k[A]^{1/3}$ .

a) What is the order of the reaction and the units of  $k$ ?

b) Initially there is pure A at a concentration  $[A]_0$ . Derive an expression for  $[A]$  as a function of time  $t$ .

c) What is the half life, for this reaction?

a)  $1/3$  order, units of  $k$  are  $M^{2/3} s^{-1}$

$$b) \quad -\frac{d[A]}{dt} = k[A]^{1/3}$$

$$\int_{[A]_0}^{[A]_t} [A]^{-1/3} d[A] = \int_0^t -k dt$$

$$\frac{3}{2} [A]^{2/3} \Big|_{[A]_0}^{[A]_t} = -kt \Big|_0^t$$

$$[A]_t^{2/3} = [A]_0^{2/3} - \frac{2}{3} kt$$

$$c) \quad \left( \frac{[A]_0}{2} \right)^{2/3} = [A]_0^{2/3} - \frac{2}{3} kt_{1/2}$$

$$\text{so } \frac{2}{3} kt_{1/2} = [A]_0^{2/3} \left( 1 - \frac{1}{2^{2/3}} \right)$$

$$\text{and } t_{1/2} = \frac{3}{2k} [A]_0^{2/3} \left( 1 - \frac{1}{2^{2/3}} \right)$$

$$\approx \frac{0.56}{k} [A]_0^{2/3}$$

(3) 20 points

How do the root-mean-square speeds and kinetic energies compare for  $\text{H}_2$  and  $\text{O}_2$  molecules at the same temperature? The molar masses are 2 g and 32 g, respectively.

$$c = \left( \frac{3k_B T}{m} \right)^{1/2}$$

$$\epsilon = \frac{3}{2} k_B T$$

Independent of mass

Kinetic energies would be equal at equal temperatures.

$$T = \frac{c^2 m}{3k_B} \quad \text{so} \quad \epsilon = \frac{3}{2} k_B \frac{c^2 m}{3k_B} = \frac{1}{2} c^2 m$$

$$\frac{1}{2} c_{\text{H}_2}^2 M_{\text{H}_2} = \frac{1}{2} c_{\text{O}_2}^2 M_{\text{O}_2}$$

$$\rightarrow c_{\text{H}_2} = 4 c_{\text{O}_2}$$