

EXAM 4

December 2, 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 possibly useful information:

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad N_A = 6.022 \times 10^{23} \text{ mol}^{-1} \quad k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ atm} = 101325 \text{ Pa}$$

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

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

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

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

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

(1) 20 points

What is the ratio of the root-mean-square speeds and kinetic energies of He and O₂ molecules at 298 K? The molar masses are 4 g and 32 g, respectively. If one mol of O₂ effuses from a container in 4 hours, how long will it take one mol of He under the same conditions?

Kinetic energy $\propto T$ \therefore same for He and O₂, 1:1.

$KE = \frac{1}{2}mc^2$ $\therefore c \propto \frac{1}{\sqrt{m}}$ \therefore O₂ moves more slowly by a factor of

$$\frac{1}{\sqrt{4}} \div \frac{1}{\sqrt{32}} = \frac{1}{2} \div \frac{1}{4\sqrt{2}} = 2\sqrt{2} \sim 2.83 \quad \text{ie. } c_{\text{He}} : c_{\text{O}_2} = 1 : \frac{1}{2\sqrt{2}} \text{ or } 1 : 0.354$$

Graham's Law of Effusion: rate $\propto c \propto \frac{1}{\sqrt{m}}$

\therefore He will effuse faster by a factor of $2\sqrt{2}$.

$$\frac{4 \text{ hr}}{2\sqrt{2}} = \sqrt{2} \text{ hr} \sim 1.41 \text{ hr}$$

(2) 40 points

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

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 of A for this reaction?

a) Order = $2/3$. $M s^{-1} = k \text{ units} \times M^{2/3} \therefore k \text{ units} = M^{1/3} s^{-1}$

b)
$$-\frac{d[A]}{dt} = 2v = 2k[A]^{2/3} \therefore \int [A]^{-2/3} d[A] = \int -2k dt$$

$$\therefore 3[A]^{1/3} = -2t \cdot k + \text{const.}$$

When $t=0$, $[A] = [A]_0 \therefore \text{const} = 3[A]_0^{1/3}$

$$\therefore [A]^{1/3} = -\frac{2kt}{3} + [A]_0^{1/3}$$

c) When $t = t_{1/2}$, $[A] = [A]_0/2 \therefore \frac{[A]_0^{1/3}}{2^{1/3}} = -\frac{2}{3}kt_{1/2} + [A]_0^{1/3}$

$$\therefore \frac{2}{3}kt_{1/2} = [A]_0^{1/3} \left(1 - \frac{1}{2^{1/3}}\right) \approx [A]_0^{1/3} \cdot 0.206$$

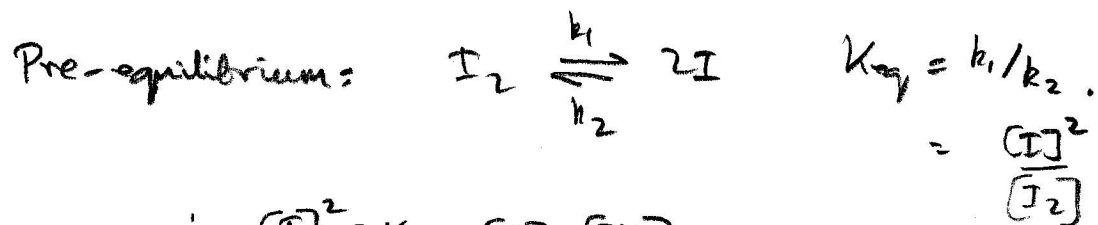
$$\therefore t_{1/2} = \frac{[A]_0^{1/3}}{k} \cdot 0.309$$

(3) 40 points

In the 1890s, experiments on the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g})$ showed that the rate law is first order in each of the reactants and second order overall. It was thought to be an elementary reaction. New experiments in the 1960s led to proposal of the mechanism



Assume that reactions 1 and 2 are much faster than reactions 3 and 4 and therefore yield a pre-equilibrium, and that the steady-state assumption applies to IH_2 , to obtain the overall rate law from this mechanism.



$$\therefore [\text{I}]^2 = K_{\text{eq}} \cdot [\text{I}_2] = \frac{[\text{IH}_2][\text{I}_2]}{k_2}$$

$$\frac{d[\text{IH}_2]}{dt} = 0 = k_3 [\text{I}][\text{H}_2] - k_4 [\text{I}][\text{IH}_2]$$

$$v = \frac{1}{2} \frac{d[\text{HI}]}{dt} = k_4 [\text{I}][\text{IH}_2] = k_3 [\text{I}][\text{H}_2] = k_3 \sqrt{\frac{k_1}{k_2}} \cdot [\text{I}_2]^{1/2} \cdot [\text{H}_2]$$
