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Track and Field – Kinetics Practice Problems

Rate Laws

1. Consider the reaction: $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$

The following data were obtained from three experiments using the method of initial rates:

	Initial [NO] mol L^{-1}	Initial $[O_2]$ mol L^{-1}	Initial rate NO mol $L^{-1}s^{-1}$
Experiment 1	0.010	0.010	2.5×10^{-5}
Experiment 2	0.020	0.010	1.0×10^{-4}
Experiment 3	0.010	0.020	5.0×10^{-5}

a. Determine the order of the reaction for each reactant.

$$\frac{2.5\times10^{-5} = \cancel{k}[0.01]^x[0.01]^y}{1\times10^{-4} = \cancel{k}[0.02]^x[0.01]^y}$$

$$0.25 = 0.5^x \Rightarrow \boxed{x=2}$$

$$\frac{2.5\times10^{-5} = \cancel{k}(0.01)^x(0.01)^y}{5\times10^{-5} = \cancel{k}(0.01)^x(0.02)^y}$$

$$0.5 = 0.5^y \Rightarrow \boxed{1 = y}$$

b. Write the rate equation for the reaction.

$$Rate = k[NO]^2[O_2]^1$$

c. Calculate the rate constant.

$$2.5\times10^{-5} = k(0.01)^2(0.01)$$

$\frac{Mol}{L\cdot s}$

$$\boxed{25\ M^{-2}\cdot s^{-1}}$$

d. Calculate the rate (in mol $L^{-1}s^{-1}$) at the instant when [NO] = 0.015 mol L^{-1} and $[O_2]$ = 0.0050 mol L^{-1}

$$Rate = (25)(0.015)^2(0.005)$$

$$\boxed{Rate = 2.8\times10^{-5}}$$

2. The reaction of ᵗbutyl-bromide $(CH_3)_3CBr$ with water is represented by the equation:

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

The following data were obtained from three experiments using the method of initial rates:

	Initial $[(CH_3)_3CBr]$ mol L^{-1}	Initial $[H_2O]$ mol L^{-1}	Initial rate mol $L^{-1}min^{-1}$
Experiment 1	5.0×10^{-2}	2.0×10^{-2}	2.0×10^{-6}
Experiment 2	5.0×10^{-2}	4.0×10^{-2}	2.0×10^{-6}
Experiment 3	1.0×10^{-1}	4.0×10^{-2}	4.0×10^{-6}

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a. What is the order with respect to $(CH_3)_3CBr$?

$$\frac{2\times10^{-6}}{4\times10^{-6}} = \frac{\cancel{k}(5\times10^{-2})^x \cancel{(2\times10^{-2})^0}}{\cancel{k}(1\times10^{-1})^x \cancel{(2\times10^{-2})^0}}$$

$$0.5 = 0.5^x \Rightarrow x = 1$$

b. What is the order with respect to H_2O?

$$y = 0$$

c. Write the rate equation.

$$\text{Rate} = k[(CH_3)_3CBr]^1[H_2O]^0$$

d. Calculate the rate constant, k, for the reaction.

$$2\times10^{-6} = k(5\times10^{-2})^1(2\times10^{-2})^0$$

$$\boxed{4\times10^{-5}\ s^{-1} = k}$$

Integrated Rate Laws

3. For the reaction 2A → 2B + C, the following data were collected:

Time (s)	[A] (M)
10	8.23×10^{-3}
20	6.74×10^{-3}
30	5.52×10^{-3}
40	4.52×10^{-3}
50	3.70×10^{-3}
60	3.03×10^{-3}

a. Determine the rate law $\text{Rate} = k[A]^x$

$$\text{Rate} = -\frac{1}{2} \cdot \frac{(6.74\times10^{-3}) - (8.23\times10^{-3})}{20 - 10} = 7.45\times10^{-5}\ M/s$$

$$\text{Rate} = -\frac{1}{2} \cdot \frac{\quad}{30 - 20} = 6.1\times10^{-5}$$

$$\boxed{\text{Rate} = k[A]^1}$$

$$\frac{7.45\times10^{-5}}{6.1\times10^{-5}} = \frac{\cancel{k}[8.23\times10^{-3}]^x}{\cancel{k}[6.74\times10^{-3}]^x}$$

$$1.22$$

$$1.22 = 1.22^x$$

$$\boxed{x = 1}$$

b. Calculate k.

$$\frac{6.1\times10^{-3}}{6.74\times10^{-3}} = \frac{k(6.74\times10^{-3})^1}{6.74\times10^{-3}} \rightarrow \boxed{k = 0.91\ s^{-1}}$$

c. Calculate the ½ life of this reaction

$$\frac{8.23\times10^{-3}}{2} = 4.115\times10^{-3}$$ ½ life [A]

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.91} = \boxed{0.76\ s}$$

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d. Calculate the [A] after 70 s.

$\ln[A] = -(0.91)(\frac{ }{10}) + \ln(3.03 \times 10^{-3})$

$\ln[A] = -14.899$

$\boxed{[A] = 3.3 \times 10^{-7}\ M}$

4. For the reaction A → product, the first two half-times are 10 minutes and 20 minutes respectively. At the beginning of the reaction, [A] was 0.10M. What is the [A] at t = 80 min?

$t_{1/2} = 10$ min

8 ½ lives

$0.1 \div 2 \div 2 \div 2 \div 2 \div 2 \div 2 \div 2 \div 2 =$

$\boxed{3.9 \times 10^{-4}\ M}$

5. The rate law for the hydrolysis of sucrose is Rate = $k[C_{12}H_{22}O_{11}]$. After 2.57 hours at 25 °C, 0.55 M of $C_{12}H_{22}O_{11}$ has decreased to 0.45 M. Calculate the rate constant value and units for this reaction.

$\ln(0.45) = -k(2.57\ h) + \ln(0.55)$

$-0.799 = -k(2.57) - {}^{-}0.598$

$\frac{-0.201}{-2.57} = \frac{-k(2.57)}{-2.57} \Rightarrow \boxed{k = 0.078\ h^{-1}}$

6. The rate constant for the second order decomposition of nitrogen dioxide,

$NO_2 \rightarrow NO + ½\, O_2$

is 3.40 $M^{-1}min^{-1}$. Calculate the time, in minutes, needed to decrease the concentration from 2.00 M to 1.50 M.

$\frac{1}{1.50} = (3.4)(t) + \frac{1}{2}$

$\frac{0.167}{3.4} = \frac{(3.4)(t)}{3.4} \Rightarrow \boxed{0.049\ min = t}$

Arrhenius Equation

7. Determine the value of k if a reaction has an activation energy of 75.5 kJ/mol and Arrhenius constant of 95.5 $M^{-1}s^{-1}$ at a temperature of 20 °C.

$\ln k = -\frac{E_a}{RT} + \ln A$

$\ln k = -\frac{(75{,}500\ J/mol)}{(8.314)(293.15)} + \ln(95.5)$

$\ln k = -30.98 + 4.56 = -26.4$

$\ln k = -26.4$

$e^{\ln k} = e^{-26.4}$

$\boxed{3.3 \times 10^{-12}\ s^{-1} = k}$

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8. Determine the value of E_a and A for the following data. Furthermore, create an Arrhenius plot and show how to use it to determine E_a, A, and k.

Temperature (K)	k (M^{-1} s^{-1})
600	0.028
650	0.22
700	1.3
750	6.0
800	23

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

$$\ln\left(\frac{0.028}{0.22}\right) = -\frac{E_a}{8.314\ J/mol\cdot K}\left(\frac{1}{650} - \frac{1}{600}\right)$$

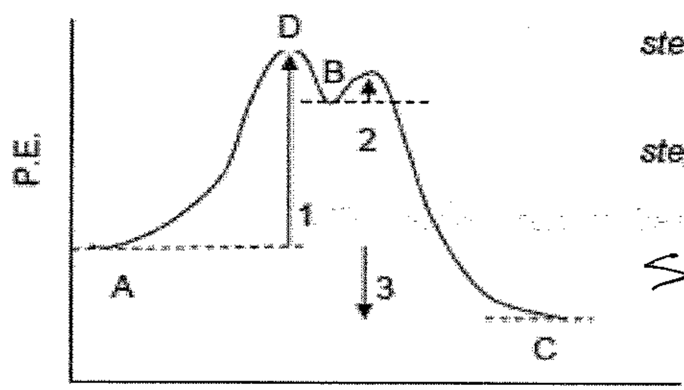
$$-6.67 = -\frac{E_a}{8.314}\left(-1.28\times10^{-4}\right)$$

$$\frac{-55.45}{1.28\times10^{-4}} = \frac{E_a(1.28\times10^{-4})}{1.28\times10^{-4}}$$

$$\boxed{E_a = 4.3\times10^{5}\ J/mol}$$

Reaction Mechanisms

9.



step 1 $H_2C{=}CH_2 + H^+ + Cl^- \rightarrow H_3C\text{-}\overset{\oplus}{C}H_2 + Cl^-$

step 2 $H_3C\text{-}\overset{\oplus}{C}H_2 + Cl^- \rightarrow H_3C\text{-}CH_2Cl$

a. Which is the rate determining step?

Step 1; E_A is higher

b. Is this reaction endo or exothermic?

Exothermic; A is higher energy than C

c. Which chemical species are present at A?

$H_2C{=}CH_2$, H^+ and Cl^-

d. Which chemical species are present at B?

$H_3C\text{-}CH_2$ and Cl^-

e. Which chemical species are present at C?

$H_3C\text{-}CH_2Cl$

f. Which chemical species are present at D? Intermediate of (A) and (B) speciacies.

g. What is the rate law for this reaction?

$$Rate = k[H_2C{=}CH_2]^1[H^+]^1$$