

## Kinetics Review Sheet

The kinetics material covers two chapters. This sheet reviews mostly the first chapter (at least in terms of practice problems). Please also see “Reaction Mechanisms Worksheet” for practice problems from the second chapter.

The “Equation Sheet” below will be exactly what you’ll see on the exam. Please note that the thermodynamic quantities in the last two lines should have the symbol  $\ddagger$ . (These may also be accidentally left off the final equation sheet.)

### Kinetics Equation Sheet

$$\begin{array}{lll} \frac{1}{([A]_0 - [B]_0)} \ln \left( \frac{[B]_0[A]_t}{[A]_0[B]_t} \right) = kt & [A]_t = [A]_0 e^{-kt} & \ln \frac{[A]_t}{[A]_0} = -kt \\ \frac{1}{[A]_t} = \frac{1}{[A]_0} + 2kt & [A]_t = [A]_0 - kt & k = A e^{-E_a/RT} \\ k = e^2 \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-E_a^\ddagger / RT} & E_a = \Delta H^\ddagger + 2RT & E_a = RT + \Delta H^\ddagger \\ k = e \frac{k_B T}{h} e^{\Delta S^\ddagger / R} e^{-E_a^\ddagger / RT} & & \end{array}$$

### Key Concepts from Kinetics

1. Orders of reaction and half-lives
2. Units of k
3. Methods of Initial Rates and Isolation
4. Kinetics and relationship to Equilibrium
5. Arrhenius Equation (and meaning of A and  $E_a$ )
6. Transition State Theory
7. Obtaining a rate expression from a given mechanism
  - a. Steady-state approximation
  - b. Fast Equilibrium
  - c. Rate Determining Steps
  - d. Chain Reactions
  - e. Catalysis (including enzyme catalysis)

**Practice Problems (Ch 28; See Mechanisms Worksheet and Key for Ch 29)**

1. For the reaction  $4A(g) + 3B(g) \rightarrow 2C(g)$ , the following data were obtained at constant temperature:

Experiment	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial Rate (mol/L·min)
1	0.100	0.100	5.00
2	0.300	0.100	45.0
3	0.100	0.200	10.0
4	0.300	0.200	90.0

- What is the order with respect to each reactant?
  - Write the rate law. What is the order of the reaction?
  - Calculate  $k$ . Give with the appropriate units.
2. In a first order decomposition reaction, 50.0% of a compound decomposes in 10.5 min.
- What is the rate constant of the reaction?
  - How long does it take for 75% of the compound to decompose?
3. The rate constant of a reaction is  $4.7 \times 10^{-3} \text{ s}^{-1}$  at 25 °C, and the activation energy is 33.6 kJ/mol.
- What is the value of  $k$  at 75 °C?
  - Calculate the values of  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  at 75 °C. Assume a unimolecular gas-phase reaction.
4. Decide if the following statements are true or false. If false, correct so they are true.
- Mechanisms are proven by collecting experimental evidence.
  - Mechanisms can be published and accepted after experimental verification of some steps.
5. Describe the Arrhenius pre-exponential,  $A$ , in words.

### Practice Problems (Related to Ch 28), Key

1a.

$$v = k[A]^m[B]^n$$

$$\frac{5.00}{45.0} = \frac{k[0.100]^m[0.100]^n}{k[0.300]^m[0.100]^n} \quad \text{or} \quad \frac{1}{9} = \left(\frac{1}{3}\right)^m$$

$$m = 2$$

$$\frac{5.00}{10.0} = \frac{k[0.100]^2[0.100]^n}{k[0.100]^2[0.200]^n} \quad \text{or} \quad \frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$n = 1$$

b.  $v = k[A]^2[B]$ , Reaction is 3<sup>rd</sup> order.

c.  $5 = k[0.100]^2[0.100]$   
 $k = 5000 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$  or  $k = 5000 \text{ dm}^6 \cdot \text{mol}^{-2} \cdot \text{min}^{-1}$

2a.  $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$  where  $[A]_t = 0.5[A]_0$

$$\ln\left(\frac{0.5[A]_0}{[A]_0}\right) = -k(10.5)$$

$$k = 0.066 \text{ 1/min}$$

b.  $\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$  where  $[A]_t = 0.25[A]_0$

$$\ln\left(\frac{0.25[A]_0}{[A]_0}\right) = -0.066t$$

$$t = 21.0 \text{ min}$$

3a.  $k = Ae^{-E_a/RT}$  or  $A = k / e^{-E_a/RT}$

So ...  $A = 3646$  1/s

$k(75^\circ\text{C}) = Ae^{-E_a/RT} = 3646e^{-33600/8.314 \cdot 348} = 3.3 \times 10^{-2}$  1/s

b.  $\Delta H^\ddagger = E_a - RT = 30.7$  kJ/mol

$$\Delta S^\ddagger = R \ln \left( \frac{Ah}{ek_B T} \right) = 1.54 \times 10^{-9} \text{ J/mol}\cdot\text{K}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger = 30.7 \text{ kJ/mol}$$

4. Decide if the following statements are true or false. If false, correct so they are true.

a. Mechanisms are proven by collecting experimental evidence. **FALSE**

**TRUE:** Mechanisms can not be proven but experimental evidence can disprove a mechanism.

b. Mechanisms can be published and accepted after experimental verification of some steps. **FALSE**

**TRUE:** Mechanisms can be published and accepted after experimental verification of all proposed steps.

5. The Arrhenius pre-exponential  $A$  is a measure of **rate at which collisions occur** (and takes lots of things into acct such as orientation, molecular size, number of molecules per volume, molecular velocity, etc).