

Chapter 14:

(1) Rate of reaction:

A) Consider the reaction: $2 \text{NH}_4\text{NO}_3 (\text{s}) \rightarrow 2 \text{N}_2 (\text{g}) + 4 \text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g})$. (Express answers on a per minute basis)

If the rate at which nitrogen gas is formed is 3.0×10^{-2} moles per minute, determine the following:

- i) the reaction rate, v_{rxn} . ii) the rate at which ammonium nitrate is used up. iii) the rate at which oxygen is formed. iv) the rate at which water is formed. (final answers in moles/min). (v) How many grams of water is formed per minute? (MW of $\text{H}_2\text{O} = 18.0 \text{g/mol}$).

(2) Mechanisms:

A) Consider an elementary step: $2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$.

- i) Write the rate law for this elementary step.
ii) What is the rate expression for the reverse of this step?
iii) what is the molecularity of this step?

B) Consider the hypothetical reaction mechanism below and predict the rate law.

Elem. Step #1 (slow) $\text{NO}_2 + \text{F}_2 + \text{Pt}(\text{s}) \rightarrow \text{FNO}_2 + \text{F-Pt}(\text{s})$

Elem. Step #2 (fast) $\text{NO}_2 + \text{F-Pt}(\text{s}) \rightarrow \text{FNO}_2 + \text{Pt}(\text{s})$

- i) what is the rate determining step? ii) What is the overall stoichiometric equation?
iii) Write the rate equation for the rate-determining step, iv) Write the rate law for this reaction. v) Is there an intermediate? vi) is there a catalyst?

C) The postulated mechanism for the decomposition of ozone is:

$\text{O}_3(\text{g}) \rightleftharpoons \text{O}_2(\text{g}) + \text{O}(\text{g})$ (fast, equilibrium)

$\text{O}(\text{g}) + \text{O}_3(\text{g}) \rightarrow 2 \text{O}_2(\text{g})$ (slow)

Determine the following:

- a) the rate law predicted by this mechanism.
b) the order of the reaction as predicted by the rate law.
c) the effect of increasing $[\text{O}_2]$ on the reaction rate.
d) an example of a change that could lead to favoring the forward reaction.

(3) Draw an energy diagram showing an endothermic reaction showing the activation energy (E_a). Label what would represent the ΔH and ΔE in your diagram. Show effect of catalyst. Which direction does a catalyst speed up?

(4) Suppose a reaction triples its rate constant when the temperature is raised from 20°C to 40°C .

- a) What is its activation energy? (in kJ/mol)
b) If its $k=3.5$ (in arbitrary units), what is its rate constant when $T = 55^\circ\text{C}$?
c) If an enzyme speeds up this reaction 100,000-fold at 37°C , what would its activation energy be equal to?

Chapter 15: Chemical Equilibrium

1) Consider the reaction mechanism for ozone depletion: (i) $O_3 \rightleftharpoons O_2 + O$, (ii) $O_3 + O \rightarrow 2O_2$,

a) What is the net reaction? Are there intermediates involved? Catalysts?

b) Write the equilibrium expression for the net reaction, in terms of concentration.

c) Write the equilibrium expression in terms of the rate constants of the elementary steps.

2) Consider the following hypothetical reaction (in an airtight container):



a) Write down the equilibrium constant EXPRESSION for this reaction.

b) The system is at equilibrium with concentrations: $[A] = 0.1M$, $[C] = 1M$, $[E] = 0.2M$. What is the VALUE of

the equilibrium constant?

c) Which direction is favored if the system initially at equilibrium is changed by increasing the following:

(i) container's volume. (ii) container's temperature. (iii) $[E]$. (iv) an inert gas (pumped into the container). (v) A substance F (i.e. F separately reacts with C). (vi) B. (vii) D. (viii) a catalyst is added.

3) Practice the use of Henry's Law: for example, homework problem 15-79.

4) For the gas phase dissociation of phosphorus pentachloride to phosphorus trichloride and elementary chlorine the value of K at 573K is 2.0. If a sample of phosphorus pentachloride is heated to 573K at a constant total pressure of 5.00 atm calculate the partial pressures of all components of the resulting mixture at equilibrium. (Involves a QUADRATIC!).

5) When molecular bromine is heated it dissociates into bromine atoms. A sample of bromine of mass 0.57g is placed in a 1.00L quartz flask and heated to 1823K and the total pressure at equilibrium is found to be 0.75 atm. Calculate K at 1823K.

6) If a 1.00g sample of calcium carbonate is placed in a 10.0L flask and heated to 1000K it is found that 1.00 mg of the calcium carbonate decomposes. Calculate K for the decomposition reaction.