# reaction rates and equilibrium

Name: ______________________________________ Period: _____
.

altering Reaction Rates

Introduction:

Chemical reactions occur at different rates. The combustion of methane is a relatively fast reaction, while the rusting of iron is quite slow. In general we would like to make the rusting of iron proceed as slowly as possible. On the other hand, an explosives chemical company might want to speed up the reactions that produce the explosives they sell. In order to understand how the rates of chemical reaction can be controlled, it is necessary to understand the collision theory of chemical reactions.

collision theory

A chemical reaction involves bond breaking and bond forming. The states that, in order to react, molecules must collide with each other with sufficient force and the correct positioning to break old bonds and form new ones. The minimum energy that the colliding molecules must have for the reaction to occur is called the activation energy. According to the collision theory, any factor that increases the number of molecular collisions that occur, or that increases the amount of energy with which the molecules collide, will increase the rate of the reaction.

In this experiment, you will study the effect of temperature, concentration of reactants, particle size and surface area on the rates of chemical reactions. You will also investigate the effect that catalysts have on reaction rates. Catalysts are substances that provide a path of lower activation energy for reactions without being consumed.

Objective: To observe the effects of temperature, concentration, particle size, surface area and catalysts on the rates of chemical reactions.

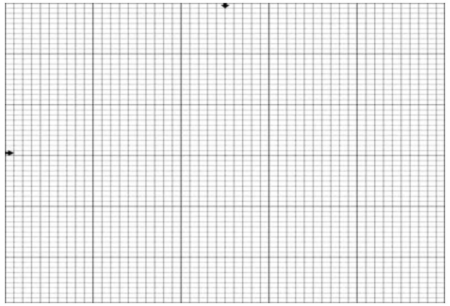
Pre-lab questions:

1. Predict the effect of temperature, concentration, and particle size on the rate of a reaction

2. An enzyme is an example of a catalyst: a substance that increases the rate of a chemical reaction without being consumed. Based on the collision theory, draw a picture of a how an enzyme might work.

Station One: The effect of temperature on reaction rate

1. You have available magnesium, 6M HCl, ice water, and hot water. In one sentence describe your experiment.



2. Make a table of your data and carefully graph your results.

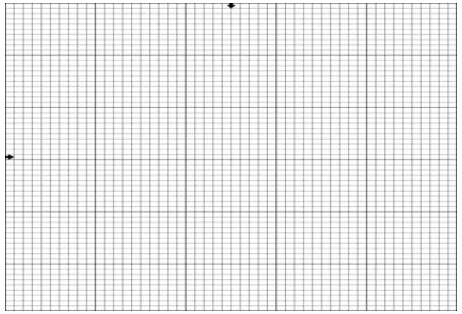
3. Write a balanced chemical equation for the reaction between hydrochloric acid and Magnesium. (Hint: It is a single replacement reaction, and Mg forms a +2 cation

4. Describe in your own words the effect of temperature on the rate of a reaction.

**Station Two: The effect of reactant concentration on reaction rate.**

6. You have available magnesium, and HCl of various concentrations. In one sentence describe your experiment.

7. Make a table of your data and carefully graph your results.



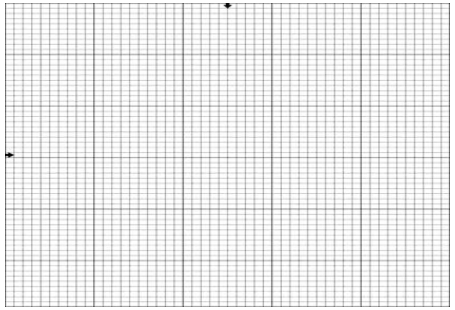
8. Describe in your own words the effect of concentration on the rate of a reaction.

9. Explain this effect in terms of the collision theory.

## Station Three: The effect of surface area on reaction rate.

10. You have available several metals of various shapes and sizes, a mortar and pestle, a pair of scissors, and hot plate capable of magnetic stirring. Note that stirring a solution will effectively increase the surface area of the reactants. In one sentence describe your experiment.

11. Tabulate your data and graph your results:



12. Write a balanced chemical equation for the reaction between hydrochloric acid and aluminum. (Hint: It is a single replacement reaction, and Al forms a +3 cation

13. Describe in your own words the effect of surface area on the rate of a reaction.

14. Explain this effect in terms of the collision theory.

## Station Four: The effect of a catalyst on reaction rate.

You have available a computer with access to the internet. Provide examples of three chemical reactions whose rate of reaction may be increased by the use of a catalyst. Do not attach any printouts.

15. Inorganic chemical reaction

Write a balanced chemical equation:

Catalyst(s):

16. Organic chemical reaction

Write a balanced chemical equation:

Catalyst(s

17. Biological chemical reaction

Describe this reaction, or write a balanced chemical equation:

18. Describe in your own words the effect of a catalyst on the rate of a reaction.

19. Explain this effect in terms of the collision theory.

Conclusions:

20. Of the various methods for increasing the rate of reaction, which do you believe can have the greatest effect and why?

21. You may have observed non-linear graphs. Explain this observation- what does it mean on a molecular level?

# reaction rates

how can we measure the rate of a reaction?

$$A \rightarrow B$$

reactant concentration decreases

product concentration increases

the speed (rate) of a reaction is like the speed of anything else (a car, for example):

$$\text{rate} = \frac{\text{change}}{\text{time}}$$


example: miles/hour

For a chemical reaction:

$$\text{rate} = \frac{\Delta \text{concentration}}{\Delta \text{time}} = \frac{M}{s}$$

[ ]= concentration in moles/liter

consider:

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + HOH$$

$[Ca(OH)_2]$ at time = 0: 0.22 M

$[Ca(OH)_2]$ after four seconds 0: 0.100 M

what is the reaction rate for $Ca(OH)_2$?

$$\frac{0.12\ M}{4\ s} = \frac{0.030\ M}{s}$$

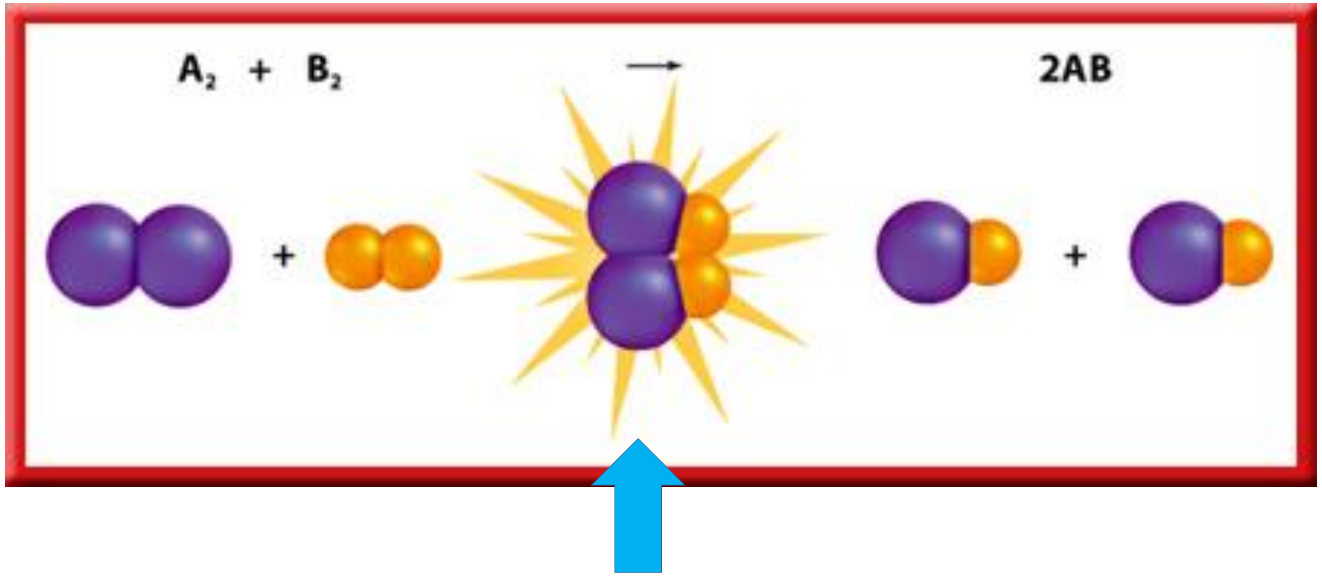
what is the reaction rate for HCl?

$$\frac{0.060\ M}{s}$$

(since two HCl molecules must react for each $CaCl_2$ molecule)

# how do molecules react?

kinetic molecular theory (kmt)




transition state
or
activated complex

suggests a reaction mechanism (process)

collision theory:

they collide
with enough force to react
and at the right location

applying KMT
5 ways to change the rate of reaction

hit it with a STICC!

change the

Surface area

Temperature

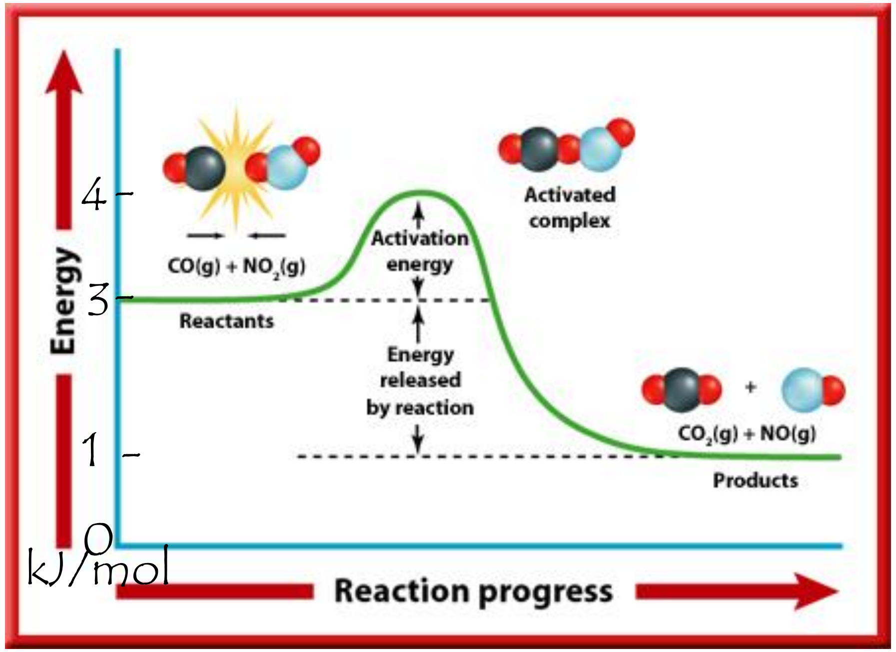
rule of thumb: rate doubles every 10 °C

Identity (of reactants)

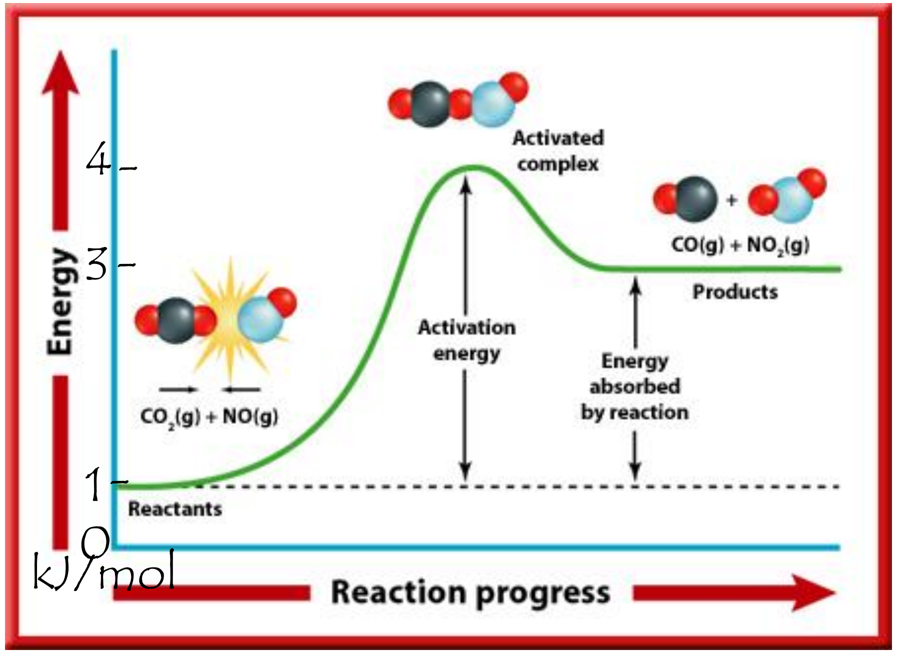
Concentration (of reactants)

add a Catalyst

# collision theory: energy diagrams

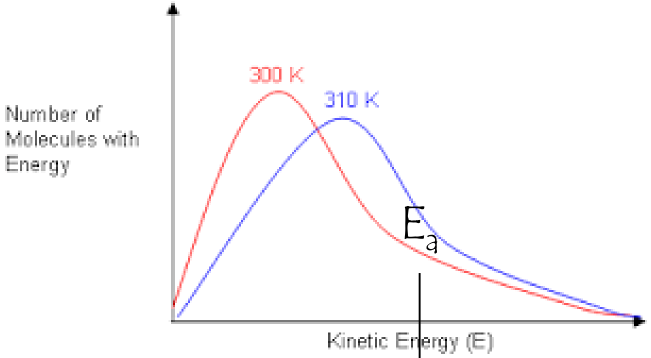



exothermic




endothermic

| exothermic | | endothermic |
|---|---|---|
| 1 kJ/mol | activation energy forward reaction: | 3 kJ/mol |
| 3 kJ/mol | activation energy reverse reaction: | 1 kJ/mol |
| -2 kJ/mol | $\Delta H_{forward}$: | +2 kJ/mol |
| +2 kJ/mol | $\Delta H_{reverse}$: | -2 kJ/mol |

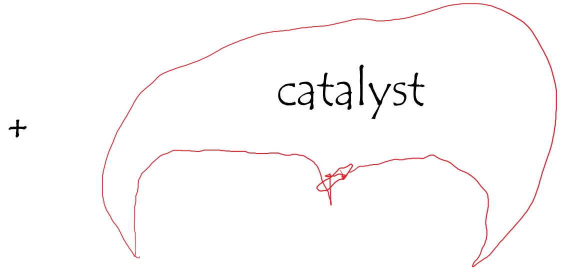



Increasing temperature increases the kinetic energy of molecule sand their energy variation, leading to more molecules that can overcome the activation energy barrier. Ths is known as a Boltzmann distribtion

a highly efficient method to increase rate of reaction without increasing temperature: lower the activation energy

# catalysts

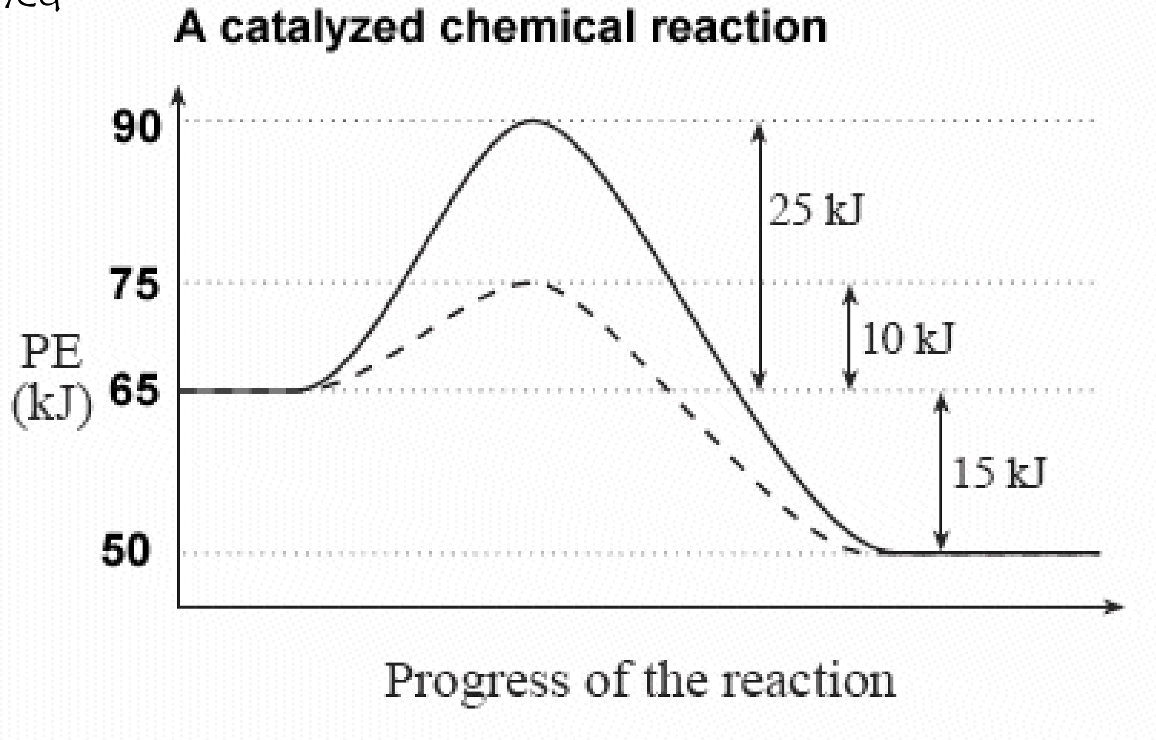





aligns molecules, catalyst not consumed

way better pathway: new mechanism with lower $E_a$

can be heterogeneous (separate phase) or homogeneous (dissolved)



# rate law:

Shows how the rate depends on the concentrations of reactants.

three outcomes are likely:
1. no effect
2. a proportional effect
3. an exponential effect

For the decomposition of nitrogen dioxide: $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

Rate = $k[NO_2]^n$, where k = rate constant and n = reactant order

if there is no effect then n = 0, if it is proportional n = 1, if exponential n = >1

3 most common errors:

- assume reaction rates are predictable (only determined by experiment)
- assume reaction orders are from reaction coefficients (they aren't)
- assume product concentrations are part of rate law formula (they aren't)

derive the rate law for 6A + 17B → 2C + 4D + 8E

rate = $k[A]^m[B]^n$ where the overall reaction order = m + n

# determining rate law: the method of initial rates

## A + B → products

| Trial | Initial [A] (*M*) | Initial [B] (*M*) | Initial Rate (mol/(L·s)) |
|---|---|---|---|
| 1 | 0.100 | 0.100 | $2.00 \times 10^{-3}$ |
| 2 | 0.200 | 0.100 | $2.00 \times 10^{-3}$ |
| 3 | 0.200 | 0.200 | $4.00 \times 10^{-3}$ |

doubling [A] has no effect on rate

doubling [B] doubles rate

this reaction is zero$^{th}$ order with respect to A, first order with respect to B, and it is first order overall.

| experimental initial rates for C + D → products | | | |
|---|---|---|---|
| trial | initial [C] in moles/liter | initial [D] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | 0.6 | 0.3 | 0.08 |
| 3 | 0.6 | 0.6 | 0.16 |

rate = k[C][D]

| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | 0.6 | 0.3 | 0.04 |
| 3 | 0.6 | 0.6 | 0.16 |

rate = $k[A]^0[B]^2$

| experimental initial rates for E + F → products | | | |
|---|---|---|---|
| trial | initial [E] in moles/liter | initial [F] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | 0.6 | 0.3 | 0.08 |
| 3 | 0.6 | 0.6 | 0.64 |

rate = $k[E][F]^3$

# the arrhenius equation

activation energy can be calculated since it depends on rate and temperature.

$$E_a = \frac{(\ln\frac{K_1}{K_2})R}{\frac{1}{T_2}-\frac{1}{T_1}}$$

k = rate constant

$E_a$: activation energy in J/mol

R =8.314 J/K mol

T = Kelvin temp

At 650 K nitrogen dioxide decomposes into nitrogen monoxide and oxygen with a rate constant of 1.66/sec. At 700K the rate constant is 7.39/sec. Calculate the activation energy

$$E_a = \frac{(\ln\frac{1.66/s}{7.39/s})(8.314\ J/K\ mol)}{\frac{1}{700K}-\frac{1}{650K}}$$

$$E_a = 113\ kJ/mol$$

# between topics concept: net ionic equations

## what really happens in a chemical reaction

consider:

__$CuCl_2$ (aq) + _2_NaOH (aq) → $Cu(OH)_2$(s) + 2 NaCl(aq)

What really reacted?? Write the ionic equation

$Cu^{2+}$ (aq) + 2$Cl^-$(aq) + 2$Na^+$(aq) + 2$OH^-$(aq) + $H_2O$(l) → $CuCl_2$(s) + 2$Na^+$(aq) + 2$Cl^-$ (aq) + $H_2O$(l)

most ions did not react! cross out the spectator ions or solvents and write the net ionic equation

$Cu^{2+}$ (aq) + 2$OH^-$(aq) + $H_2O$(l) → $Cu(OH)_2$(s)

this is: what really happened

it is misleading to some because ions are always paired

noting that group 1 ions and nitrates are always soluble, write the net ionic equation for the reactions of

1. potassium phosphate with calcium nitrate

2 _2_ $K_3PO_4$ + _3_ $Ca(NO_3)_2$ → _6_ $KNO_3$ + _1_ $Ca_3(PO_4)_2$ (s)

answer: 3 $Ca^{2+}$ (aq) + 2 $PO_4^{2-}$ (aq) → $Ca_3(PO_4)_2$ (s)

2. sodium hydroxide with magnesium nitrate

__NaOH + _1_ $Mg(NO_3)_2$ → _2_ $NaNO_3$ + _1_ $Mg(OH)_2$ (s)

answer: $Mg^{2+}$ (aq) + 2 $OH^-$ (aq) → $Mg(OH)_2$ (s)

really useful shortcut:

look for the precipitate!

# Equilibrium:

= reversibility

chemical reactions are often reversible:

$$aA + bB \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftharpoons}} cC + dD$$

chemical equilibrium: forward rate = reverse rate

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

the "equilibrium constant

<1: mostly reactants (bad) >1: mostly products (good)

generally: omit liquids and solids

write the equilibrium expression

$$H_2(g) + I_2(g) \leftrightarrows 2HI(g)$$

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]}$$

$$FeO(s) + CO\,(g) \leftrightarrows Fe(s) + CO_2\,(g)$$

$$K_{eq} = \frac{[CO_2]}{[CO]}$$

$$2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g);\ K_{eq} = 0.00227$$

If $[S_2] = 0.0540$ mol/L and $[H_2S] = 0.184$ mol/L, what is $[H_2]$?

$$K_{eq} = 0.00227 = \frac{[H_2]^2\ [S_2]}{[H_2S]^2} = \frac{[H_2]^2[0.054]}{[0.184]^2}$$

$$[H_2] = 0.0377 \text{ moles/liter}$$

if the actual ratio of products to reactants (Q) is <K the reaction will proceed forward; if the measured concentrations are >K the reaction will shift to the left until it matches the equilibrium concentrations

# reaction ratios help solve equilibrium problems

1. $Fe^{3+}(aq) + SCN^-(aq) \leftrightarrows FeSCN^{2+}(aq)$

6.00 M $Fe^{3+}(aq)$ and 10.0 M $SCN^-(aq)$ are mixed at a constant temperature. At equilibrium the concentration of $FeSCN^{2+}(aq)$ is 4.00 M.

What is the $K_{eq}$?

| | | | |
|---|---|---|---|
| initial M | | | |
| change M | | | |
| equilibrium M | | | |

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = \frac{[4.00]}{[2.00][6.00]}$$

$$= 0.333$$

2. $CH_3CO_2H\ (aq) + CH_3CH_2OH(aq) \leftrightarrows CH_3CO_2CH_2CH_3(aq) + \cancel{H_2O}(l)$

acetic acid — ethanol — ethyl acetate — water

An aqueous solution of ethanol and acetic acid, each at a concentration of 0.810 M, is heated to 100. degrees Celsius. At equilibrium, the acetic acid concentration is 0.748. Calculate $K_{eq}$ for the reaction.

| | | | |
|---|---|---|---|
| | | | |
| initial M | | | |
| change M | | | |
| equilibrium M | | | |

$$K_{eq} = \frac{[CH_3CO_2CH_2CH_3]}{[CH_3CO_2H][CH_3CH_2OH]} = \frac{[0.062]}{[0.748][0.748]} = 0.111$$

3. A tank of $H_2S$ at a pressure of 10.00 atm and constant temperature is decomposing:

$$2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g)$$

When the reaction has come to equilibrium, the partial pressure of $S_2$ (g) is 0.020 atm. Calculate $K_p$.

partial pressures work just like molarity

| | | | |
|---|---|---|---|
| initial atm | | | |
| change atm | | | |
| equilibrium atm | | | |

$$K_p = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[0.040]^2[0.020]}{[9.96]^2} = 3.2 \times 10^{-7}$$

# try these two equilibrium problems

$$X(g) + Y(g) \leftrightarrows 2Z(g)$$

When 4.00 mol each of X(g) and Y(g) are placed in a 1.00L vessel and allowed to react at constant temperature according to the equation above, 6.00 mol of Z(g) is produced. What is the value of the equilibrium constant Kc?

| | X (g) + | Y (g) $\leftrightarrows$ | 2Z (g) |
|---|---|---|---|
| initial M | 4 | 4 | 0 |
| change M | – 3 | – 3 | + 6 |
| equilibrium M | 1 | 1 | 6 |

$$k_c = \frac{(6)^2}{(1)(1)} = \mathbf{36}$$

The war gas phosgene ($COCl_2(g)$) decomposes according to the equation shown:

$$COCl_2(g) \leftrightarrows CO(g) + Cl_2(g)$$

When pure phosgene is injected into a rigid, previously evacuated flask at 690K the pressure in the flask is initially 1.00 atm. After the reaction reaches equilibrium at 690K, the total pressure in the flask is 1.2 atm. What is the value of $K_p$ for the reaction at 690K?

| | $COCl_2$ $\leftrightarrows$ | CO + | $Cl_2$ |
|---|---|---|---|
| initial atm | 1 | 0 | 0 |
| change atm | – x | + x | + x |
| equilibrium atm | 1 – x | + x | + x |

$$P_{total} = P_{COCl2} + P_{CO} + P_{Cl2}$$

$$1.2\text{ atm} = 1 - x + x + x$$

$$1.2\text{ atm} = 1 + x$$

$$x = 0.2\text{ atm}$$

| | | | |
|---|---|---|---|
| initial atm | 1 | 0 | 0 |
| change atm | – 0.2 | + 0.2 | + 0.2 |
| equilibrium atm | 0.8 | 0.2 | 0.2 |

$$k_p = \frac{(0.2)(0.2)}{(0.8)} = \mathbf{0.050}$$

# equilibrium constants can be combined

$a \leftrightarrows b$   $k_c = \frac{[b]1}{[a]1} = 3$

what is k for $b \leftrightarrows a$?

$k = \frac{1}{3}$

what is K for $2a \leftrightarrows 2b$

$k = 3^2 = 9$

$a \leftrightarrows b$
$k = 3$
$b \leftrightarrows c$
$k = 5$
----------
what is k for $a \leftrightarrows c$?

$k = 15$

summarize:

reverse = inverse
double = square
add = multiply

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1. Given
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$   $K_1 = 0.212$ @ 100°C?
Find $K_2$
$2\ NO_2(g) \leftrightarrows N_2O_4(g)$ at 100° C   $K_2 = ?$

$K_2 = 1/K_1 = 1/0.212 = 4.72$

2. Given:
$1/2 I_2(g) + 1/2\ Cl_2\ (g) \leftrightarrows ICl(g)$   $K_1 = 4.54 \times 10^2$ @ 25°C
Find, at the same temperature, $K_2$
$2\ I_2(g) + 2\ Cl_2(g) \leftrightarrows 4\ ICl(g)$

$K_2 = K_1^4 = (4.54 \times 10^2)^4 = 4.25 \times 10^{10}$

3. Given:
$2\ N_2\ (g) + O_2(g) \leftrightarrows 2\ N_2O(g)$   $K_1 = 1.2 \times 10^{-35}$   reverse
$N_2O_4(g) \leftrightarrows 2\ NO_2(g)$   $K_2 = 4.6 \times 10^{-3}$   reverse and double
$1/2N_2(g) + O_2(g) \leftrightarrows NO_2(g)$   $K_3 = 4.1 \times 10^{-9}$   quadruple
Find $K_4$
$2\ N_2O(g) + 3\ O_2(g) \leftrightarrows 2\ N_2O_4(g)$   $K_4 = ?$

$$\begin{array}{lll}
2\ N_2O(g) & \leftrightarrows & \cancel{2\ N_2(g)} + \cancel{O_2(g)} \\
\cancel{4\ NO_2(g)} & \leftrightarrows & 2\ N_2O_4(g) \\
\cancel{2\ N_2(g)} + \overset{3}{\cancel{4}}\ O_2(g) & \leftrightarrows & \cancel{4\ NO_2(g)} \\
\hline
2\ N_2O(g) + 3\ O_2(g) & \leftrightarrows & 2\ N_2O_4(g)
\end{array}$$

$K = 1/(1.2 \times 10^{-35}) = 8.3 \times 10^{34}$
$K = 1/(4.6 \times 10^{-3})^2 = 4.7 \times 10^4$
$K = (4.1 \times 10^{-9})^4 = 2.8 \times 10^{-34}$

$K_4 = (8.3 \times 10^{34})(4.7 \times 10^4)(2.8 \times 10^{-34}) = 1.1 \times 10^6$

# le chatelier's principle

$$A\,(g) + 3B\,(g) \leftrightarrows C\,(g)$$
$$\Delta H = +30 \text{ kcal/mole}$$

| change | result | why |
|---|---|---|
| add reactant | → | "stoking the fire" |
| add product | ← | "quenching the fire" |
| heat | → | it needs it (endothermic; $\Delta H > 0$) |
| pressurize | → | product has fewer moles ($1 < 4$) |

equilibrium can be adjusted by changing concentrations, temperature, or pressure.

$$2NO(g) + O_2(g) \leftrightarrows 2NO_2(g)$$
$$\Delta H = +250 \text{ Kcal/mol}$$

| change | shift |
|---|---|
| 1. add [NO] | → |
| 2. add [$NO_2$] | ← |
| 3. add [$O_2$] | → |
| 4. remove [NO] | ← |
| 5. remove [$NO_2$] | → |
| 6. remove [$O_2$] | ← |
| 7. increase pressure | →(3 to 2) |
| 8. increase temperature | → (endo) |
| 9. decrease pressure | ← |
| 10. decrease temperature | ← |

the best way to drive a reaction to completion is:

to remove the product as it is formed.

# rates and equilibrium

| how fast | how far |
| --- | --- |

# rates and equilibrium: problems

1. Define the following terms

A. rate of reaction (also known as reaction kinetics

B. reactant

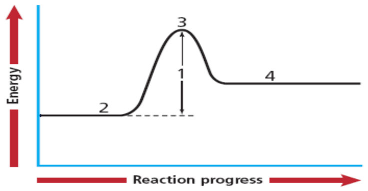
C. product

D. transition state

E. activated complex

2. What is necessary for a chemical reaction to proceed (collision theory)

3. 5 ways to change the rate of a reaction




4. Given an energy diagram such as the one at left, be able to determine:

How much energy a reaction, or the reverse reaction, needs to proceed

5. Where the transition state is

6. How exothermic or endothermic a reaction is

7. Rate of reaction given reaction time and concentration change

Example:

[HCl] at time = 0: 0.22 M

[HCl] after four seconds 0.32 M

What is the reaction rate?

8. In the energy unit we learned how to predict if a reaction will take place spontaneously. In this unit we determined how to measure how fast a reaction is. What is the relationship, if any, between reaction rate and spontaneity? To consider this, answer each question with a brief explanation

a. are fast reactions always spontaneous? Provide an example that supports and another that refutes this.

b. if the free energy of a reaction is highly positive, is it a slow reaction? Provide an example that supports and another that refutes this.

c. Are fast or spontaneous reactions dangerous? Provide an example that supports and another that refutes this.

d. Are fast reactions exothermic? Provide an example that supports and another that refutes this.

9. For the reaction $I_2$ (g) + $Cl_2$ → 2 ICl(g), the [$I_2$] changes from 0.400 M at time = 0 to 0.300 M after 4 minutes. What is the average reaction rate for $I_2$?

10. A chemical reaction is observed to occur at a rate of $2.25 \times 10^{-2}$ moles per liter per second at 322 K. What is the rate in moles per liter per minute, and moles per liter per hour?

11. Given the data below for the reaction of $H_2$ with $Cl_2$ to make HCl, calculate the average reaction rate for $H_2$, $Cl_2$, and HCl. Does it agree with the balanced chemical equation?.

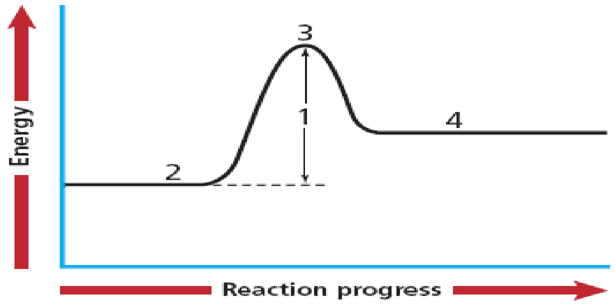
**Experimental Data for $H_2 + Cl_2 \rightarrow 2HCl$**

| Time (s) | [$H_2$] (*M*) | [$Cl_2$] (*M*) | [HCl] (*M*) |
|---|---|---|---|
| 0.00 | 0.030 | 0.050 | 0.000 |
| 4.00 | 0.020 | 0.040 | 0.020 |

12. Given the following data for the decomposition of hydrogen peroxide ($H_2O_2$), calculate the rate of reaction in moles $H_2O_2$ consumed per liter per minute for each time interval.

Initial concentration of $H_2O_2$: 3M
Concentration of $H_2O_2$ after 3 minutes: 1.3M

13. For the energy diagram below, identify positions 1-4.




14. For the reaction of nitrogen gas with hydrogen gas to make $NH_3$ (g}, if the rate of reaction with respect to loss of $N_2$ is $1/88 \times 10^{-4}$ M/s determine the rate of reaction for the other two substances.

15. In the reaction of aqueous sodium hydroxide and aqueous hydrochloric acid in a one liter flask, the concentration of NaOH changes from 2.0 M M to 1.0 M after 2 seconds., while the concentration of oxygen decreases from 3.0 M to 2.0 M over the same time interval.

a. Write the balanced chemical equation.

b. What is the reaction rate for the consumption of NaOH in this reaction?

What is the reaction rate for the consumption of HCl in this reaction?

d. Assuming the rates are steady, how long would this reaction take to go to completion?

e. How many grams of water would eventually form from this reaction

f. Would there be any remaining starting materials when this reaction is complete?

16. List six ways to increase the rate of a chemical reaction.

17. Given the following data for the decomposition of hydrogen peroxide ($H_2O_2$), calculate the rate of reaction in moles $H_2O_2$ consumed per liter per minute.

Initial concentration of $H_2O_2$: 2.6 M
Concentration of $H_2O_2$ after 3 minutes: 1.53 M

Write the rate law for the hypothetical reactions shown below; fill in the blanks when needed.

Example 1:

| experimental initial rates for $2H_2 + O_2 \rightarrow 2H_2O$ | | | |
|---|---|---|---|
| trial | initial $[H_2]$ in moles/liter | initial $[O_2]$ in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.6 | 0.3 | 0.04 |
| 2 | 1.2 | 0.3 | 0.08 |
| 3 | 0.6 | 0.6 | 0.16 |

18. rate = ____________ k = ____________

Example 2:

| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | 0.6 | 0.3 | 0.16 |
| 3 | 0.6 | 0.6 | 0.64 |

19. rate = ____________ k = ____________

Example 3:

| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.1 | 0.1 | 0.1 |
| 2 | 0.1 | 0.3 | 0.3 |
| 3 | 0.2 | 0.3 | 0.6 |

20. rate = ____________ k = ____________

Example 4:

| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | 0.9 | 0.3 | 0.04 |
| 3 | 0.9 | 4.2 | 0.04 |

21. rate = ____________ k = ____________

Example 5:

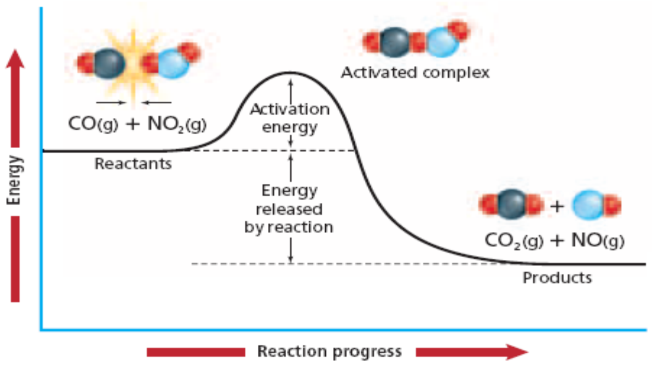
| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.3 | 0.3 | 0.04 |
| 2 | | 0.3 | 0.08 |
| 3 | 0.3 | | 0.16 |

22. rate = k[a][b] k = ____________

Example 6:

| experimental initial rates for A + B → products | | | |
|---|---|---|---|
| trial | initial [A] in moles/liter | initial [B] in moles/liter | Initial rate in moles per liter per second |
| 1 | 0.20 | 0.40 | 0.040 |
| 2 | | 0.40 | 0.16 |
| 3 | 0.20 | | 0.32 |

23. rate = $k[a]^2[b]^3$ k = ____________




22. For the energy diagram above, **what single element** is being transferred in the chemical reaction of carbon monoxide with nitrogen dioxide to form carbon dioxide and nitrogen monoxide?

23. Is the reaction above endothermic or exothermic?

24. Cut out and match the boxes in sets of 3. One set has been done for you.

| | | |
|---|---|---|
| a. Reaction rate increases when a catalyst is used | b. This means that there is a bigger area of a solid exposed, so there is a greater chance of collisions causing a reaction. | c. People dancing at a party are more likely to bump into each other than people sitting down. |
| d. Reaction rate increases when temperature is increased | e. Small particles have a greater overall area than the same amount of big particles. This means there are more particles exposed so more collisions can happen. | f. For example, If you have 100 people, they are more likely to bump into each other if in this classroom compared to a soccer field. |
| g. This explains why reaction rate increases when pressure is increased | h. Catalysts lower the 'activation energy' of a reaction, allowing it to happen with less energy input. | i. If you lower the bar in a high jump competition, more people can get over it. |
| j. Reactions go faster when the surface area is increased. | k. If particles move faster, there is more chance of them bumping into each other and therefore of a collision resulting in reaction. | k. A lot of children in a room are more likely to bump into each other than a few adults. |
| l. Rate of reaction increases when particle size gets smaller. | m. If there are more reacting particles in a given volume, then there is a greater chance of them bumping into each other. | n. French fries fry faster than potatoes because the oil can cover a bigger area |
| o. Reactions speed up when the reactants are more concentrated. | p. When reacting particles get pushed closer together so there is more chance of a successful collision happening. | q. More bumper cars at the arcade means that you are more likely to bump into someone than if there were only 2 or 3 |

Here is one answer, write the other 5. You may have to add a nice connecting word or two to make it flow.

1. When reacting particles get pushed closer together so there is a greater chance of successful collisions happening. For example, if you have 100 people, they are more likely to bump into each other in this classroom compared to a soccer field. This explains why reaction rate increases when pressure is increased.

2.

3.

4.

5

25. For the reaction of hydrogen with oxygen to make water:

$$2H_2 + O_2 \rightarrow 2H_2O$$

lining the reactants up in a column such as this

H–H
O=O
H–H

can lead to a hypothetical activated complex where all bonds are simultaneously breaking and forming. Draw this activated complex using dotted lines for each partial bond.

26. For the reaction of chalk with hydrochloric acid

$CaCO_3$ (s) + 2HC l (aq) → $CaCl_2$ (aq) + $H_2O$ (l) + $CO_2$ (g)

in an open container at room temperature the reaction is found to be exothermic, releasing 12.5 kJ/mol $CaCO_3$. Predict if the rate of reaction will increase (I), decrease (D), or remain the same for each change with a brief explanation

a. The chalk is ground into finer particles

b. More water is added to the reaction mixture.

c. The temperature is increased

d. The calcium chloride is removed from the reaction mixture as it is formed

e. A catalyst is added

27. A catalyst is discovered that lowers the activation energy of a reaction by 75 percent. Draw an energy diagram that matches this data.

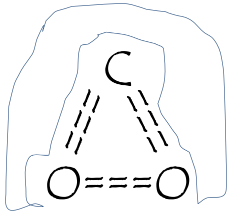
28. At 150 K an unknown diatomic substance AB decomposes into $A_2$ and $B_2$ nitrogen dioxide decomposes into nitrogen monoxide and oxygen with a rate constant of $1.4 \times 10^4$/sec. At 700K the rate constant is $7.3 \times 10^6$/sec. Calculate the activation energy

29. A reaction rate doubles when the temperature increases from 25°C to 40°C. Calculate the activation energy.

30. The activation energy for the isomerization of cyclopropane to propene is 274 kJ/mol. By what factor does the rate of reaction increase as the temperature rises from 500°C to 550°C?

Draw the balanced chemical equation, a reasonable activated complex and based on that design a catalyst for each of the reactions shown. For these examples assume the activated complex is for a single step reaction mechanism that shows all bonds breaking simultaneously (in reality multistep reaction mechanisms are common). Also, a catalyst provides a non-reactive template so that all criteria for collision theory are met. A suggested catalyst is shown for the first one

31. The reaction of carbon with oxygen to make carbon dioxide.




a. Balanced chemical equation:

b. Activated complex (show bond formation with dotted lines)

c. catalyst:

32. The reaction of magnesium with oxygen to make magnesium oxide.

a. Balanced chemical equation:

b. Activated complex (show bond formation with dotted lines)

c. catalyst:

33. The reaction of hydrogen with oxygen to make water.

a. Balanced chemical equation:

b. Activated complex (show bond formation with dotted lines)

c. catalyst:

# equilibrium problems

indicate the direction of the change in equilibrium for each change

$H_2(g) + Cl_2(g) \leftrightarrows 2HCl \quad \Delta H = -167.2$ kcal

| | equilibrium shift | [H2] | [I2] | [HI] | K |
|---|---|---|---|---|---|
| 1. add $H_2$ | | --- | | | |
| 2. add $Cl_2$ | | | --- | | |
| 3. add HCl | | | | --- | |
| 4. remove $H_2$ | | --- | | | |
| 5. remove $Cl_2$ | | | --- | | |
| 6. remove HCl | | | | --- | |
| 7. increase temperature | | | | | |
| 8. decrease temperature | | | | | |
| 9. increase pressure | | | | | |
| 10 decrease pressure | | | | | |
| 11. add a catalyst | | | | | |

35. Define chemical equilibrium

to the rate of the reverse process

36. Write equilibrium constant expressions for the following reactions. For gases use either pressures or concentrations.

a. $3\ O_2\ (g) \leftrightarrows\ 2\ O_3(g)$

b. $Fe(s) + 5CO(g) \leftrightarrows\ Fe(CO)_5(g)$

c. $(NH_4)_2CO_3(g) \leftrightarrows 2NH_3(g) + CO_2(g) + H_2O(g)$

d. $AgNO_3(aq) \leftrightarrows Ag^+\ (aq) + NO_3^-(aq)$

37. The reaction

$$2NO_2(g) \leftrightarrows N_2O_4(g)$$

has an equilibrium constant, $K_c$, of 170 at 25°C. If $2.0 \times 10^{-3}$ mol of $NO_2$ is present in a 10.liter flask along with $1.5 \times 10^{-3}$ mol of $N_2O_4$, is the system at equilibrium? If it is not at equilibrium, does the concentration of $NO_2$ increase or decrease as the system proceeds to equilibrium?

38. The reaction

$$C(s) + CO_2(g) \leftrightarrows 2CO(g)$$

occurs at high temperatures. At 700 degrees Celsius, a 2.0 liter flask contains 0.10 mol of CO, 0.20 mol of $CO_2$, and 0.40 mol of C at equilibrium.

a. calculate K for the reaction at 700 degrees Celsius

b. Calculate K for the reaction at the same temperature if the amounts at equilibrium in the 2.0 liter flask are 0.10 mol of CO, 0.20 mol of $CO_2$, and 0.80 mol of C

c. Compare the results of a and b. Does the quantity of carbon affect the value of K? Explain

39. A mixture of CO and $Cl_2$ is placed in a reaction flask. [CO] = 0.0102 mol/L and $[Cl_2]$ = 0.00609 mol/L. When the reaction

$$CO(g) + Cl_2(g) \leftrightarrows COCl_2(g)$$

has come to equilibrium at 600K, $[Cl_2)$ = 0.00301 mol/L

a. Calculate the concentrations of CO and $COCl_2$ at equilibrium

b. Calculate K

40. The equilibrium constant K for the reaction for the reaction

$$CO_2(g) \leftrightarrows CO(g) + \tfrac{1}{2}\ O_2(g)$$

is $6.66 \times 10^{-12}$ at 1000 K. Calculate K for the reaction

$$2\ CO(g) + O_2 \leftrightarrows 2CO_2(g)$$

41. Calculate K for the reaction

$$SnO_2(s) + 2CO(g) \leftrightarrows Sn(s) + 2CO_2(g)$$

given the following information

$SnO_2(s) + 2H_2(g) \leftrightarrows Sn(s) + 2H_2O(g)$  K = 8.12

$H_2(g) + CO_2(g) \leftrightarrows H_2O(g) + CO(g)$  K = 0.771

42. Dinitrogen trioxide decomposes to NO and $NO_2$ in an endothermic process($\Delta H$ = 40.5 kJ/mol).

$N_2O_3(g) \leftrightarrows NO(g) + NO_2(g)$

Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left right or no change) when each of the following changes are made:

a. adding more $N_2O_3$

b. adding more $NO_2(g)$

c. increasing the volume of the reaction flask

d. lowering the temperature

43. Consider the isomerization of butane to is butane

butane (g) $\leftrightarrows$ isobutane (g)

with an equilibrium constant of K = 2.5. The system is originally at equilibrium with [butane] = 1.0M and [isobutane] = 2.5M in a 1L flask

a. if 0.50 mol/L of isobutane is suddenly added and the system shifts to a new equilibrium position, what is the equilibrium concentration of each gas?

| | B $\leftrightarrows$ | I |
|---|---|---|
| initial atm | 1 | 3 |
| change atm | + x | − x |
| equilibrium atm | 1 + x | 3 − x |

$$k_p = \frac{3-x}{1+x} = \mathbf{2.5} \qquad x = 0.143\ M$$

| | | |
|---|---|---|
| initial atm | 1 | 3 |
| change atm | + 0.143 | −0.143 |
| equilibrium atm | **1.143** | **2.857** |

check: $k_{eq} = \frac{2.857}{1.143} = 2.5$

since Q > K (mixture is beyond eq value) reaction will reverse until equilibrium is reached

43b. if 0.50 mol/L of butane is added instead of isobutane and the system shifts to a new equilibrium position, what is the equilibrium concentration of each gas?

44. Carbon tetrachloride can be produced bu the following reaction:

$CS_2(g) + 3Cl_2(g) \leftrightarrows S_2Cl_2(g) + CCl_4(g)$

Suppose 1.2 mol of $CS_2$ and 3.6 mol of $Cl_2$ were placed in a 1.00 liter flask. At equilibrium the mixture contains 0.90 mol $CCl_4$. Calculate K

45. The equilibrium constant for the enzyme catalyzed isomerization

D-glucose ⇆ D-fructose

isomerization is 0.81 at 25 $^{o}C$.[1] If 1.75 mol of D-glucose and 1.25 mol of D-fructose are mixed and water is added so the solution has a volume of 1 liter in the presence of the enzyme, is the system at equilibrium? If not when it proceeds to equilibrium, which reagent increases in concentration? Calculate the concentrations of the two compounds when the system reaches equilibrium

46. Heating a metal carbonate is necessary to get it to decompose:

$BaCO_3(s) \leftrightarrows BaO(s) + CO_2(g)$

Predict the effect on the equilibrium for each change: left right or no change

a. add $BaCO_3$

b. add $CO_2$

c. add BaO

d. raise the temperature

e. increase the volume of the flask containing the reaction

47. Ammonium hydrogen sulfide decomposes on heating.

$NH_4HS(s) \leftrightarrows NH_3(g) + H_2S(g)$

If $K_p$ for this reaction 0.11 atm at 25°C, what is the total pressure in flask at equilibrium?

48. The equilibrium constant, $K_p$, for

$N_2O_4(g) \leftrightarrows 2NO_2(g)$

is 0.15 at 25 °C. If the pressure of $N_2O_4$ at equilibrium is 0.85 atm, what is the total pressure of the gas mixture ($N_2O_4$ + $NO_2$) at equilibrium?

49 (challenging problem). At 450 °C, 3.60 mol of ammonia is placed in a 2.00L vessel and allowed to decompose to the elements:

$2NH_3(g) \leftrightarrows N_2(g) + 3H_2(g)$

If the experimental value of K is $6.3 \times 10^{-6}$ for this reaction at this temperature, calculate the equilibrium concentration of each reagent. What is the total pressure in the flask? Since K is very low, you may assume that $(3.60 - x)^2$ in your denominator = $3.6^2$

52. $X(g) + Y(g) \leftrightarrows 2Z(g)$

When 4.00 mol each of X(g) and Y(g) are placed in a 1.00L vessel and allowed to react at constant temperature according to the equation above, 6.00 mol of Z(g) is produced. What is the value of the equilibrium constant Kc?

53. $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$

At 450 $^{o}$C, 2.0 moles each of $H_2(g)$, $I_2(g)$, and HI(g) are combined in a 1.0 L rigid container. The value of Kc at 450 $^{o}$C is 50. Which of the following will occur as the system moves forward toward equilibrium?

a. More $H_2(g)$ and $I_2(g)$ will form
b. More HI(g) will form
c. The total pressure will decrease
d. No net reaction will occur because the number of molecules is the same on both sides of the equation

# rates and equilibrium summary problem

The dissolution of calcium iodide was studied.

1. write the net ionic equation

The rate of dissolution was studied at 25 OC

| trial | [calcium iodide] | rate M/s |
|---|---|---|
| 1 | 1.0 | 3.2 |
| 2 | 2.6 | 8.32 |

2.Determine the reaction order, rate law, and rate constant

3. When the temperature is increased to 50 $^{O}C$ the rate is 6.4 M/s
Determine the activation energy.

4. The dissolution was found to have a $\Delta H$ of -4.0 KJ/mol at 25 $^{O}C$.
Draw an energy diagram, a possible activated complex, and design a catalyst for this process

5. At 25 $^{O}C$ 50% of the Calcium iodide has enough energy to overcome the activation energy, and at 50 $^{O}C$ 90% of it has sufficient energy. Show this graphically

6.The equilibrium of calcium iodide dissociation was studied at 25 $^{O}C$
The initial concentration of calcium iodide was 2.0 M and upon reaching equilibrium the concentration of iodide was found to be 1.6 M.
Determine the equilibrium constant

7. A 25 $^{O}C$, Keq for the dissolution of calcium iodate is 0.035:

$Ca(IO_3)_2 \leftrightarrows Ca^{2+} + 2\ I^- + 3O_2$ Keq = 0.035

Combine this with your data above:

$CaI_2 \leftrightarrows Ca^{2+} + 2\ I^-$ Keq =____

to determine the equilibrium constant for the synthesis of calcium iodate:

$CaI_2 + 3O_2 \leftrightarrows Ca(IO_3)_2$

8. Suggest four ways to increase the equilibrium for dissolving calcium iodide, and two methods to completely destroy it.