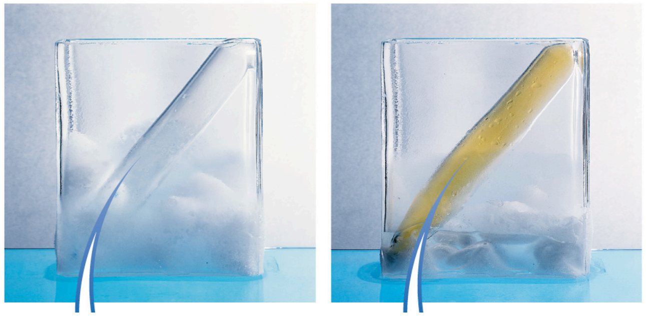
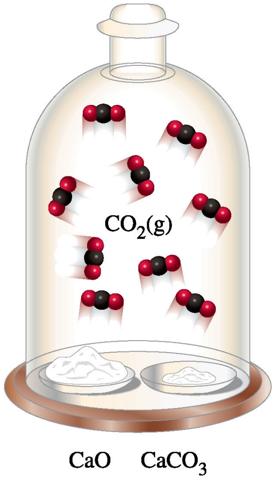
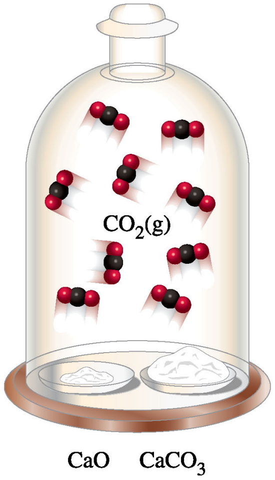
Chapter 15: Principles of Chemical Equilibrium



$$K_P = K_c(RT)^{\Delta n \text{ (gas)}}$$

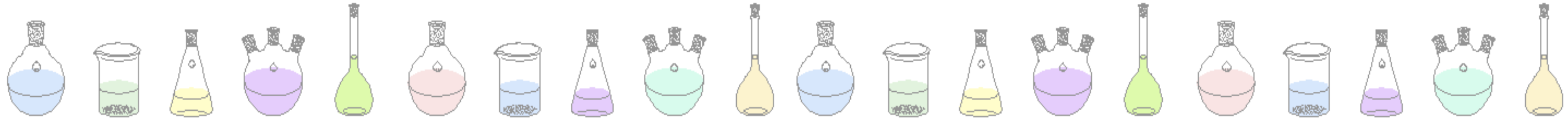




Dynamic Equilibrium

- so far, we have considered chemical reactions as having only one direction
- at a certain point, however, all reactions are reversible, i.e., the products may react to give back the reactants
- when the speeds of the forward and reverse reactions are equal, and so the concentrations of the reactants and products remain constant, equilibrium is attained

rate of forward reaction = rate of reverse reaction



The concept of equilibrium

- a ***physical equilibrium*** consists of a single substance:

$$H_2O(l) \leftrightarrows H_2O(g)$$

- a ***chemical equilibrium*** involves two or more substances:

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

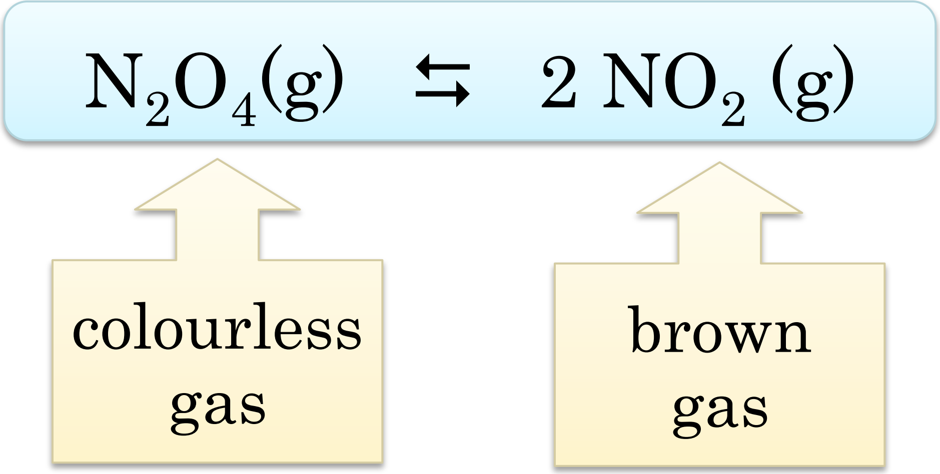
The Concept of Equilibrium

- For an equilibrium we write:

$$A \rightleftarrows B$$

- As the reaction progresses:
  - – [A] decreases to a constant
  - – [B] increases from zero to a constant
  - – When [A] and [B] are constant, equilibrium is achieved

An example: the N_2O_4/NO_2 equilibrium

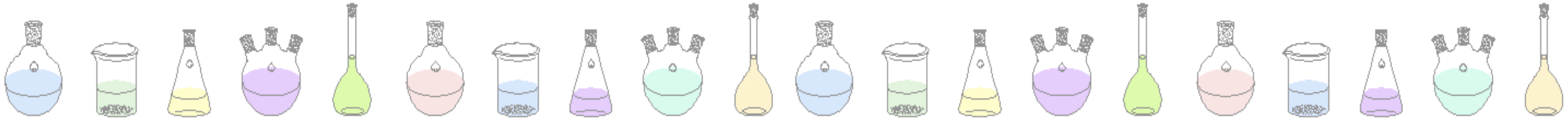


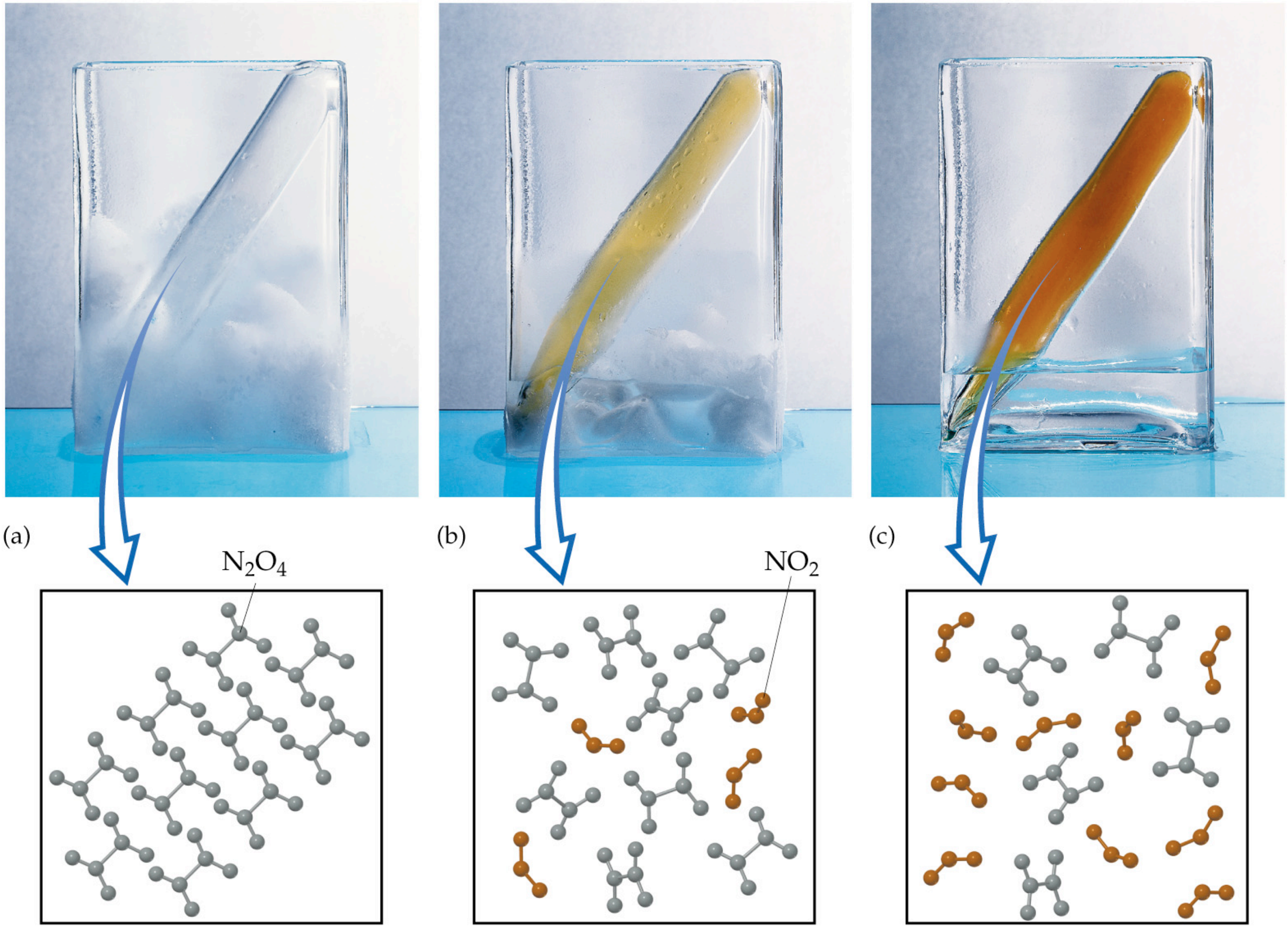
$$N_2O_4(g) \leftrightarrows 2\,NO_2\,(g)$$

colourless gas

brown gas

- Initially we have only frozen $N_2O_4(g)$ some of which reacts to form NO_2
- At some time, the colour stops changing and we have a mixture of N_2O_4 and NO_2
- Chemical equilibrium is the point at which the concentrations of all species are constant





$N_2O_4(s)$

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

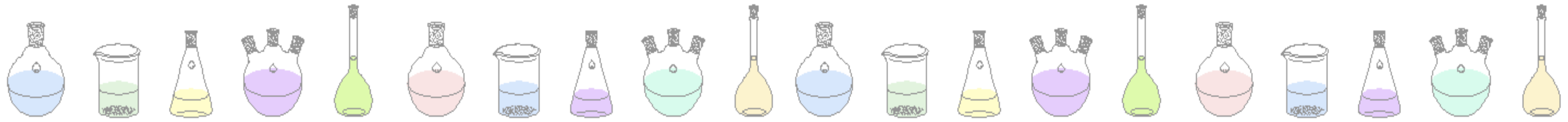
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The Concept of Equilibrium

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

Equilibrium is established when:

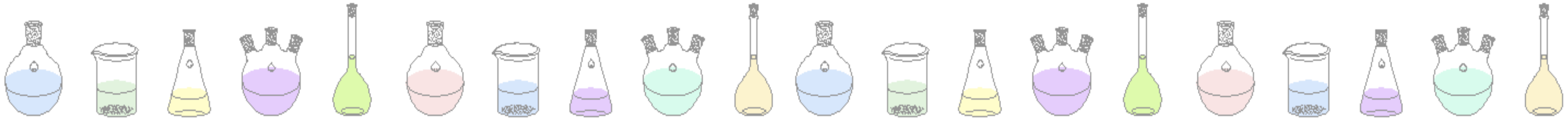
rate of forward reaction = rate of reverse reaction



The Magnitude of K

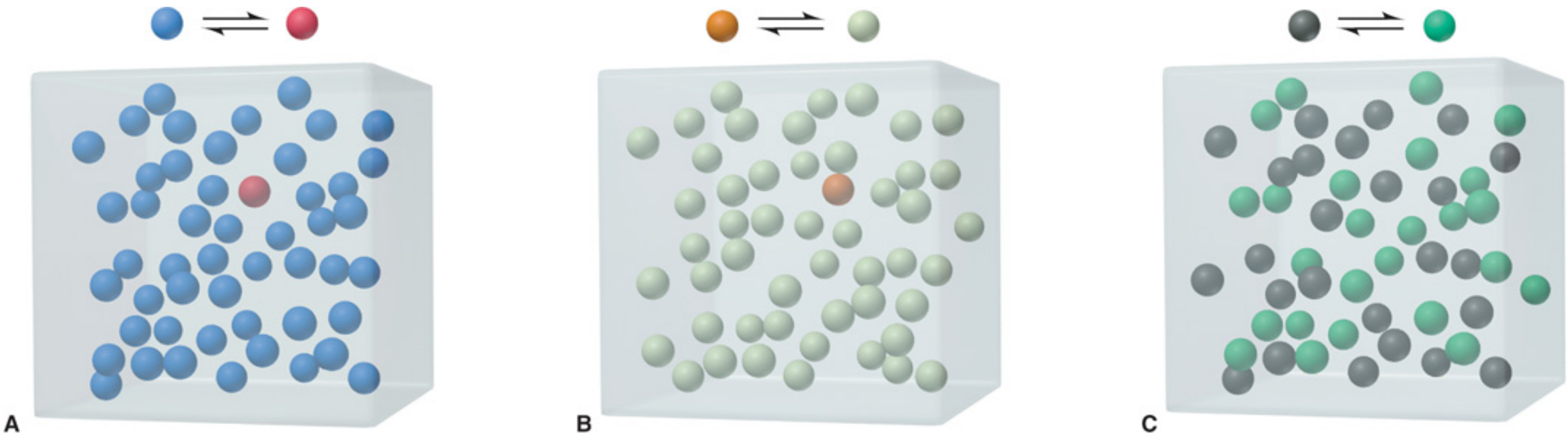
- K is the **ratio** of products to reactants
  - measure of reaction extent
- **very small K:** very little product, mostly reactant
  - "NO REACTION"
- **very large K:** mostly products, very little reactant
  - "REACTION GOES TO COMPLETION"
- **intermediate K:** significant amounts of reactant and product

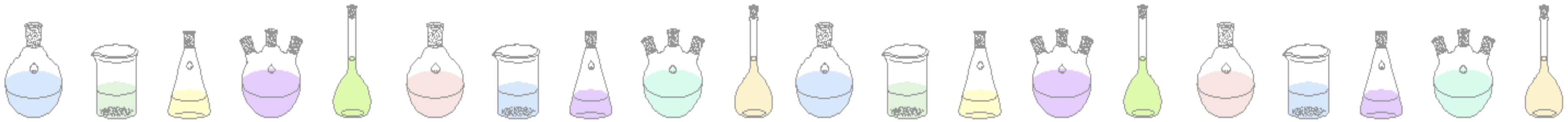
*****The same equilibrium is established no matter how the reaction begins*****



Some examples

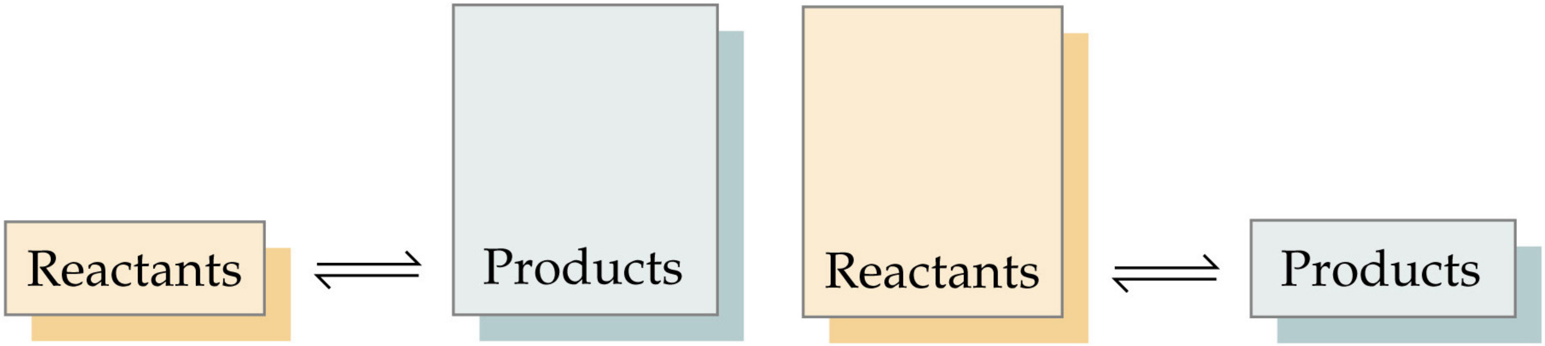
small K	large K	intermediate K
$N_2 + O_2 \leftrightarrows 2NO$	$2CO + O_2 \leftrightarrows 2CO_2$	$2BrCl \leftrightarrows Br_2 + Cl_2$
1.0×10^{-30} at 1000K	2.2×10^{22} at 1000K	5.0 at 1000K





Values of K...

Reaction	Equilibrium constant, K_p
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(l)$	1.4×10^{83} at 298 K
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	1.9×10^{-23} at 298 K 1.0 at about 1200 K
$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$	3.4 at 1000 K
$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	1.6×10^{-21} at 298 K 10.0 at about 1100 K



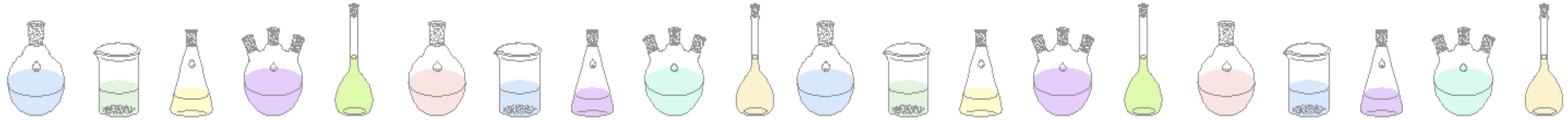
(a) $K_{eq} \gg 1$

(b) $K_{eq} \ll 1$

How large or how small?

$$A \rightleftharpoons B$$

K	mol% A	mol% B
100000	0.00	100.0
10000	0.01	99.99
1000	0.10	99.90
100	0.99	99.01
10	9.09	90.91
1	50.00	50.00
0.1	90.91	9.09
0.01	99.01	0.99
0.001	99.90	0.10
0.0001	99.99	0.01
0.00001	100.00	0.00



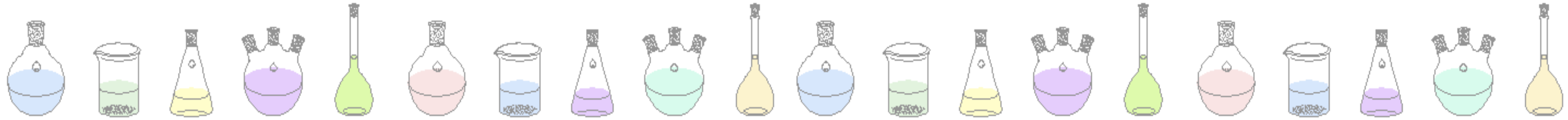
The Equilibrium Constant

- the equilibrium constant relates the concentrations of reactants and products at equilibrium
- the equilibrium constant has no units!
- for the general reaction: $aA + bB \leftrightarrows cC + dD$

$$\boxed{K = \frac{(a_C)^c(a_D)^d}{(a_A)^a(a_B)^b}}$$

- where
  - $a_x = 1$ for a solid or liquid
  - $a_x = P_x$ for a gas (in **<u>bar</u>**)
  - $a_x \approx [X]$ (in mol/L, or M) for a solute

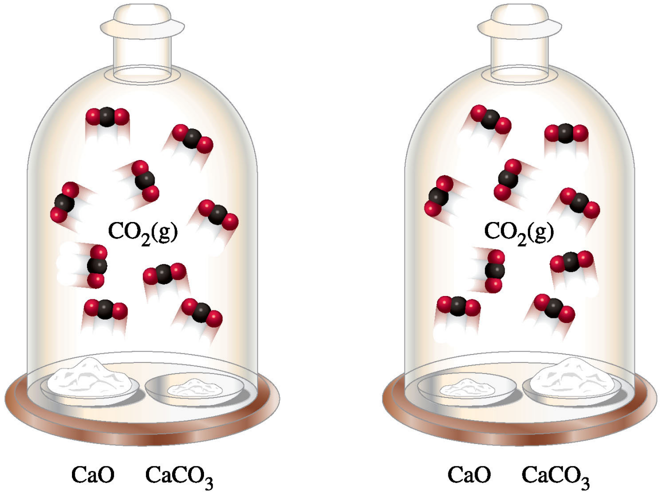
*see p. 603 for more on *activities*



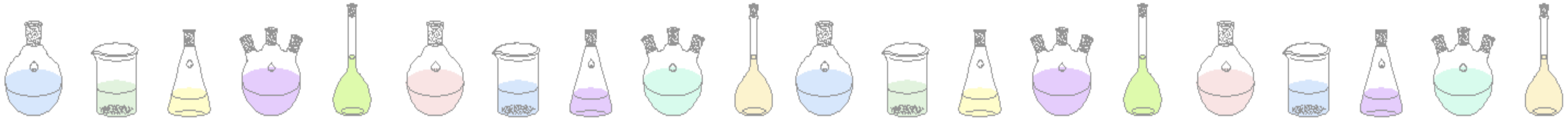
The Equilibrium Constant

- because $a_x = 1$ for a solid or liquid, we can say that their activities *do not appear* in the expression for K

$$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$$



$$K = \frac{(a_{CaO})(a_{CO_2})}{(a_{CaCO_3})} = \frac{(1)(P_{CO_2})}{(1)} = P_{CO_2}$$



Your Turn…

What is the equilibrium constant expression for the following reaction?

$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

A. $[NH_4^+][OH^-] / [NH_3][H_2O]$

B. $[NH_3][H_2O] / [NH_4^+][OH^-]$

C. $[NH_3] / [NH_4^+][OH^-]$

D. $[NH_4^+][OH^-] / [NH_3]$

E. I’m not sure

The Equilibrium Constant

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Values of K…

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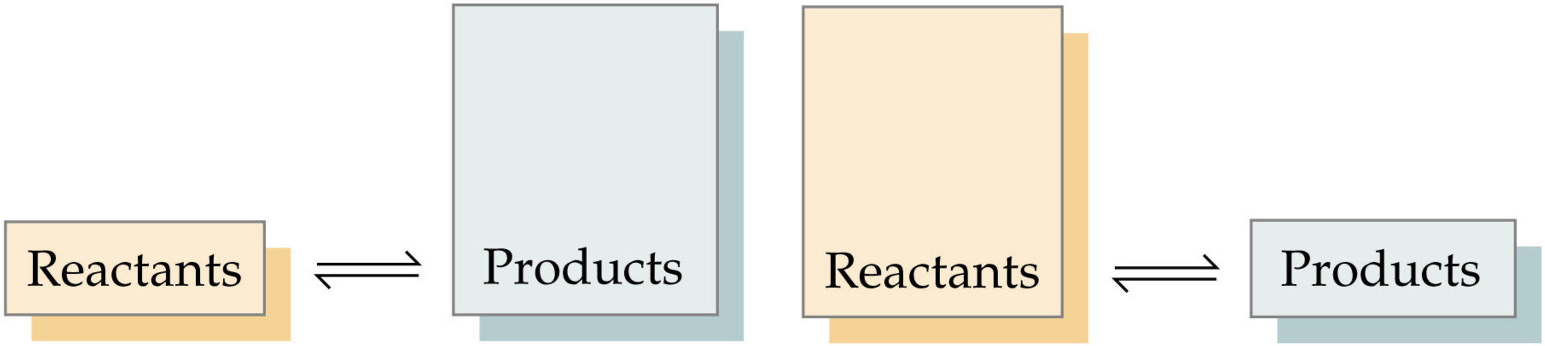
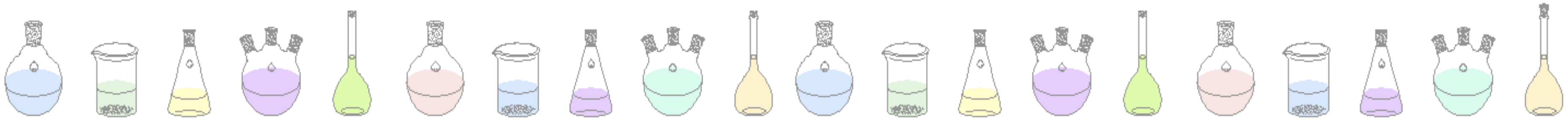


(a) $K_{eq} >> 1$

(b) $K_{eq} << 1$



Manipulating Equilibrium Constants 1

- when we multiply the coefficients in a balanced equation by a common factor **n**, we raise the value of K to the corresponding ____________:

$$2\ NO_2(g) \leftrightarrows N_2O_4(g) \qquad K = x$$

$$NO_2(g) \leftrightarrows \frac{1}{2}\ N_2O_4(g) \qquad K' = \sqrt{x}$$

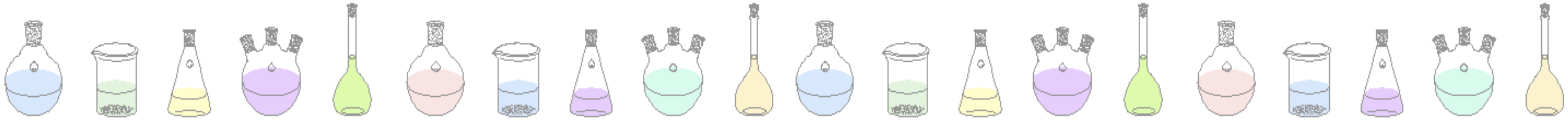
$$4\ NO_2(g) \leftrightarrows 2\ N_2O_4(g) \qquad K' = x^2$$

Manipulating Equilibrium Constants 2

- When we reverse a chemical equation, we ________ the value of K:

$$2\ NO_2(g) \leftrightarrows N_2O_4(g) \qquad K = x$$

$$N_2O_4(g) \leftrightarrows 2\ NO_2(g) \qquad K = \frac{1}{x}$$

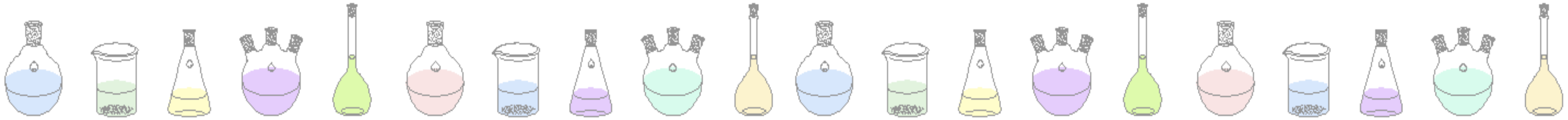


Manipulating Equilibrium Constants 3

- when adding chemical equations together, we ________________ their values of K:

$$\begin{array}{lr} 2\,\mathrm{NOCl(g)} \leftrightarrows 2\,\mathrm{NO(g)} + \mathrm{Cl_2(g)} & K_1 \\ 2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \leftrightarrows 2\,\mathrm{NO_2(g)} & K_2 \\ \hline 2\,\mathrm{NOCl(g)} + \mathrm{O_2(g)} \leftrightarrows \mathrm{Cl_2(g)} + 2\,\mathrm{NO_2(g)} & \end{array}$$

$$K_3 = K_1 \text{ x } K_2$$



Your Turn…

For the reaction $2\ A \leftrightarrows B + 3\ C$ K = 10 at 25°C

What is K for the reaction: $2\ B + 6\ C \leftrightarrows 4\ A$

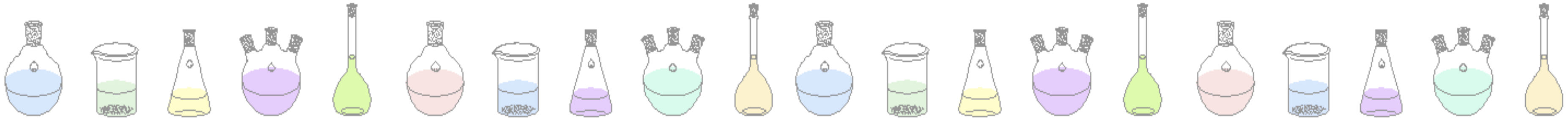
A. 10

B. 1

C. 0.1

D. 0.01

E. I'm not sure



Your Turn…

What would be the value of K at 25°C for the reaction

$$A \leftrightarrows B + C$$

given the data below at 25°C?

$A \leftrightarrows X$ $K = 10$

$B + C \leftrightarrows X$ $K = 2$

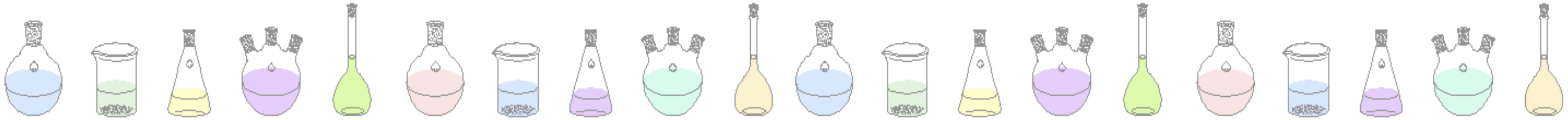
A. 20

B. 5

C. 0.5

D. 0.2

E. I'm not sure



Equilibria involving gases

$$2\ NO_2(g) \leftrightarrows 2\ NO(g) + O_2(g)$$

$$K = \frac{(P_{NO})^2(P_{O_2})}{(P_{NO_2})^2}$$

K_P = the equilibrium constant in

____

- *but*: if we know the number of moles of each gas and the volume of the container…

Equilibria involving gases

$$2\ NO_2(g) \leftrightarrows 2\ NO(g) + O_2(g)$$

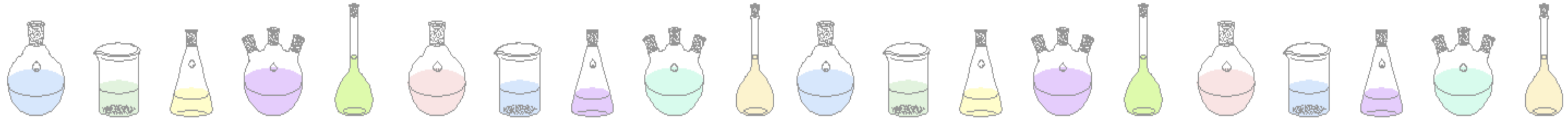
- ...we know the concentrations of each gas!

$$[NO_2] = \frac{n_{NO_2}}{V} \qquad [NO] = \frac{n_{NO}}{V} \qquad [O_2] = \frac{n_{O_2}}{V}$$

$$K = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

K_C = the equilibrium constant in

____



Can I convert between K_P and K_c?

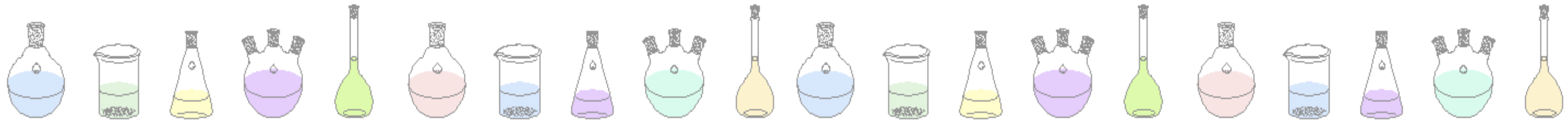
$$2\ NO_2(g) \leftrightarrows 2\ NO(g) + O_2(g)$$

We can convert between K_P and K_c with the following:

$$\boxed{K_P = K_c(RT)^{\Delta n(gas)}}$$

where $\Delta n_{(gas)}$ = change in number of moles of gas

Derivation: p 609 – 610



Example: Converting between K_P and K_c

$$H_2S(g) + I_2(s) \rightleftharpoons 2\,HI(g) + S(s)$$

At EQM:

$P = 1.01$ bar

$P = 3.70 \times 10^{-3}$ bar

T = 333 K

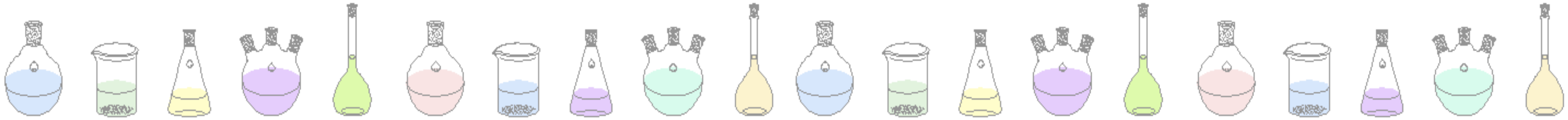
What are the values of K_P and K_c?

The Reaction Quotient, Q: Predicting the Direction of Net Change

- Consider the following reaction:

$$CO(g) + 2\ H_2(g) \rightleftarrows CH_3OH(g)$$

- How will we know the direction of change of this reaction with various starting conditions?
- Equilibrium can be approached various ways
- We need to develop a qualitative determination of change of initial conditions as equilibrium is approached



The Reaction Quotient, Q: Predicting the Direction of Net Change

- the reaction quotient, Q, is the value obtained when initial reactant activities are used in the equilibrium constant expression
- the reaction quotient for the following general reaction

$$b\,B + c\,C \leftrightarrows d\,D + e\,E$$

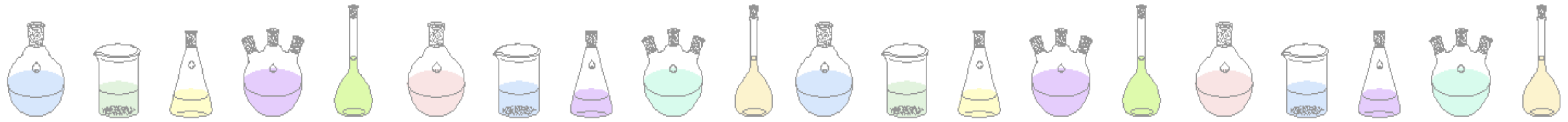
is given as:

$$Q = \frac{(a_D)^d (a_E)^e}{(a_B)^b (a_C)^c}$$

- where a_x = 1 for a solid or a liquid

= P_x for a gas (in bar)

= [X] (in mol/L) for a solute

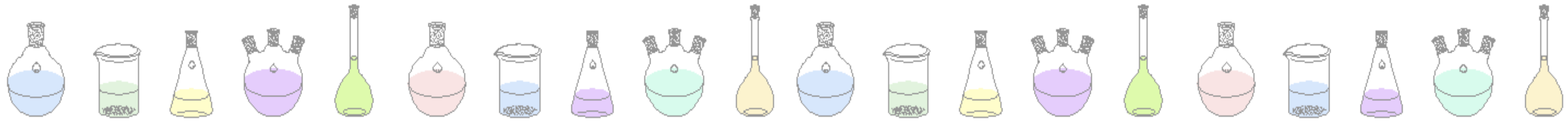


We can predict the direction of net change by comparing Q with K

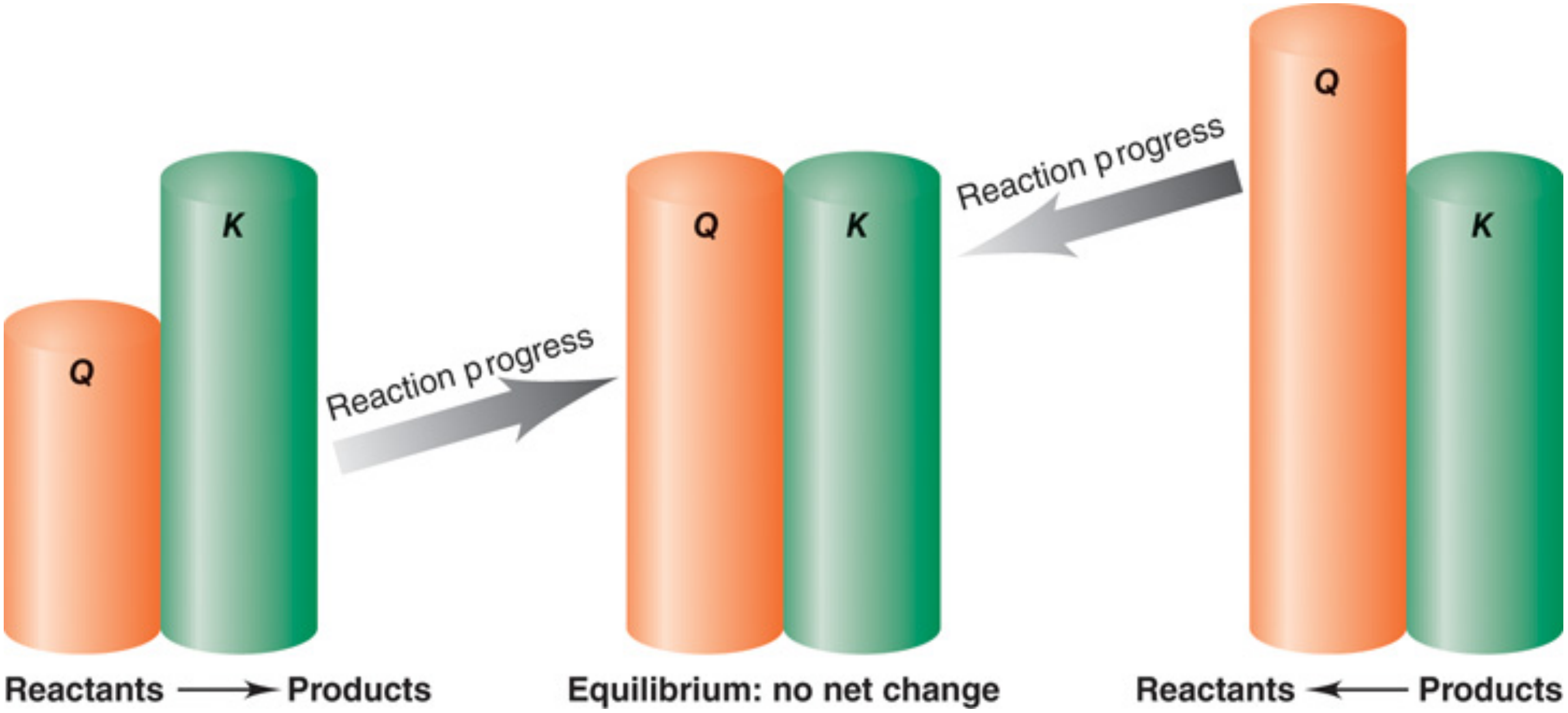
- if **Q > K**, there is an excess of products so some must react to reform reactants; thus the reaction proceeds to the __________

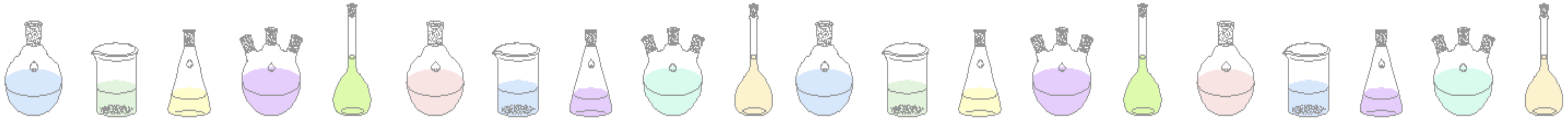
- if **Q < K**, there is an excess of reactants so some must react to form products; thus the reaction proceeds to the ___________

- if **Q = K**, the reaction is __________________(no net change in concentration)



Visual Representations of Q and K





Direction of Change: three cases

	$H_2(g)$	+	$I_2(g)$	⇆	$2HI(g)$
Initial	1.00		1.00		0

	$H_2(g)$	+	$I_2(g)$	⇆	$2HI(g)$
Initial	1.00		0		1.00

	$H_2(g)$	+	$I_2(g)$	⇆	$2HI(g)$
Initial	1.00		1.00		1.00

Your Turn…

Predict the net direction of the following reaction:

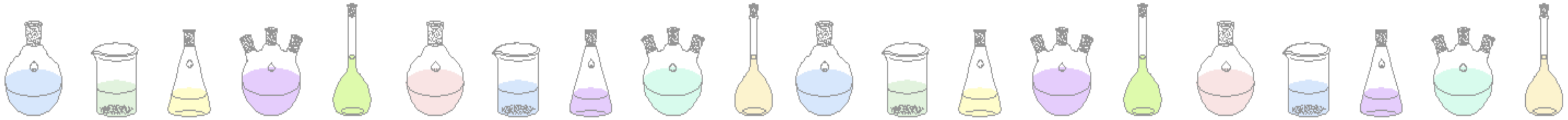
$$\begin{array}{ccccc} H_2(g) & + & I_2(g) & \leftrightarrows & 2HI(g) \qquad K = 0.0184 \\ 1.00\text{ bar} & & 1.00\text{ bar} & & 1.00\text{ bar} \end{array}$$

A. towards the reactants

B. towards the products

C. already at equilibrium

D. I don’t know



Solving Equilibrium Problems

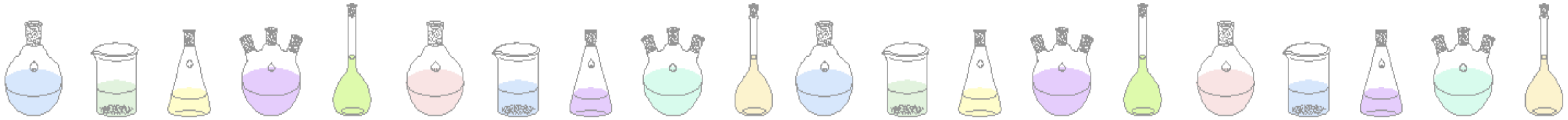
- TYPE 1 Equilibrium Problem:

initial conc. + equil. conc. → value of K

- TYPE 2 Equilibrium Problem:

initial conc. + value of K → equil. conc.

- Use ICE tables in the solution
  - TYPE 2, solving for x: quadratic equation, square root of both sides, or the simplifying assumption



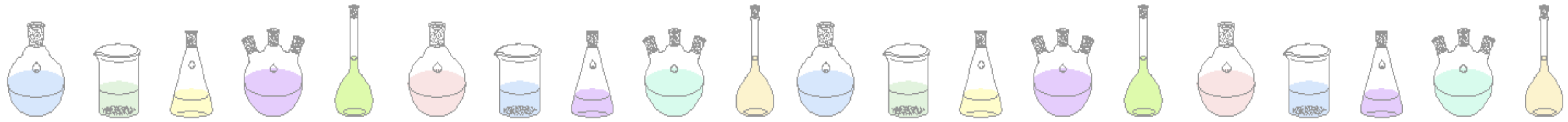
Example 1: Determining K

$$2\ \mathrm{NOCl(g)} \rightleftharpoons 2\ \mathrm{NO(g)} + \mathrm{Cl_2(g)}$$

2.00 mol of NOCl are placed in a 1.00 L flask. At equilibrium, you find 0.66 mol/L of NO. Calculate K_c.

This is a “TYPE 1” equilibrium question:

initial conc. + equil. conc. $\longrightarrow$ value of K



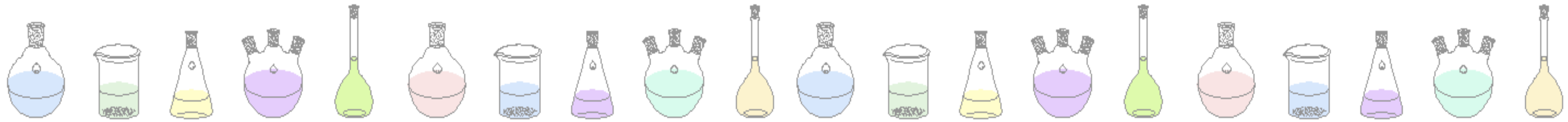
Example 2: Equilibrium concentrations

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \qquad K_C = 57.0 \text{ at } 700K$$

1.00 mol of H_2 and 1.00 mol of I_2 are placed in a 10.0 L vessel at 700K. What are the concentrations of each species at equilibrium?

This is a “TYPE 2” equilibrium problem:

initial conc. + value of K → equil. conc.



Example 3: Using Q

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g) \qquad K_P = 0.0435 \text{ at } 330K$$

1.00 mol of each gas are placed in a 10.0 L vessel at 330K. What are the partial pressures of each species at equilibrium?

This is a "TYPE 2" equilibrium problem:

initial conc. + value of K ⟶ equil. conc.

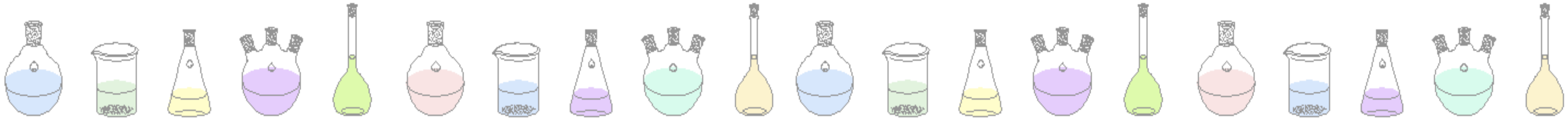
Example 4: Making the assumption

$$\mathrm{I_2(g)} \rightleftharpoons \mathrm{2I(g)} \qquad K_C = 2.94\mathrm{x}10^{-10} \text{ at } 600\mathrm{K}$$

0.50 mol of I_2 are placed in a 2.5 L vessel at 600K. What are the concentrations of each species at equilibrium?

This is a "TYPE 2" equilibrium problem:

initial conc. + value of K ⟶ equil. conc.

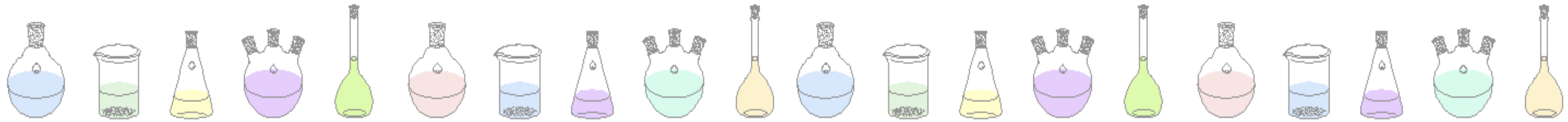


Equilibrium Conditions:
Le Châtelier's Principle

- Our approach with Q suggests a treatment for equilibrium systems that undergo a perturbation:

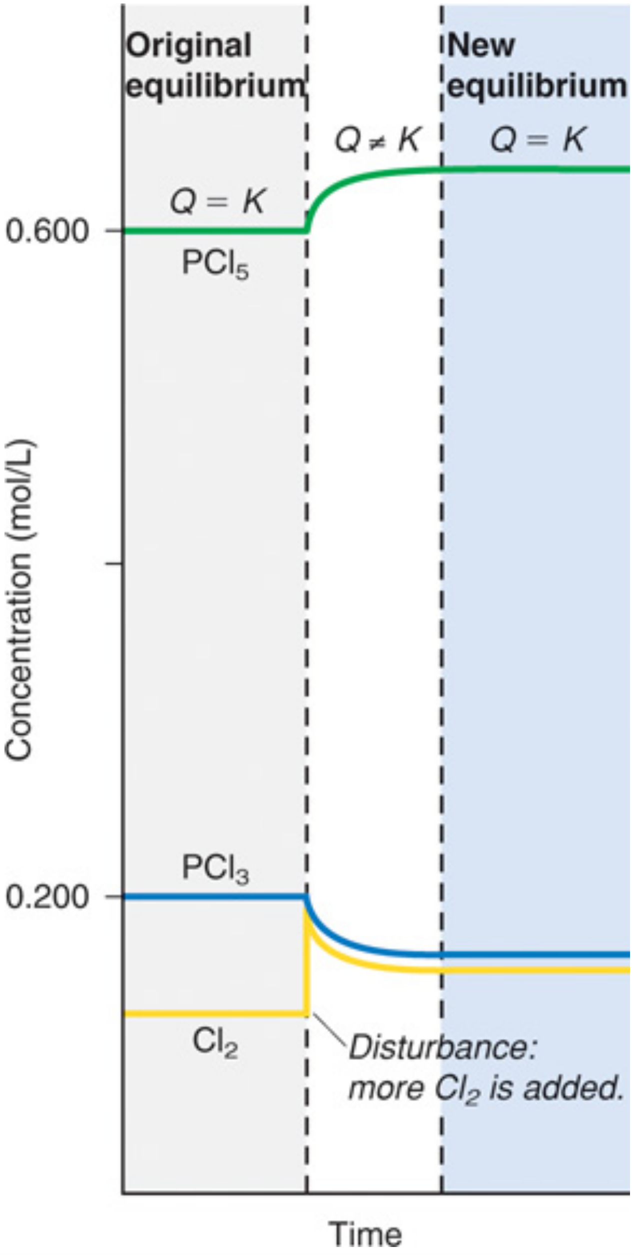
Le Châtelier's Principle

- When a system at equilibrium system is subjected to a change in temperature, pressure, or concentration of a reacting species, the system responds by attaining a new equilibrium that partially offsets the impact of the change.



1. Modifying Concentrations

$$PCl_3(g) + Cl_2(g) \leftrightarrows PCl_5(g)$$



1. Modifying Concentrations

Reactants $\rightleftharpoons$ Products

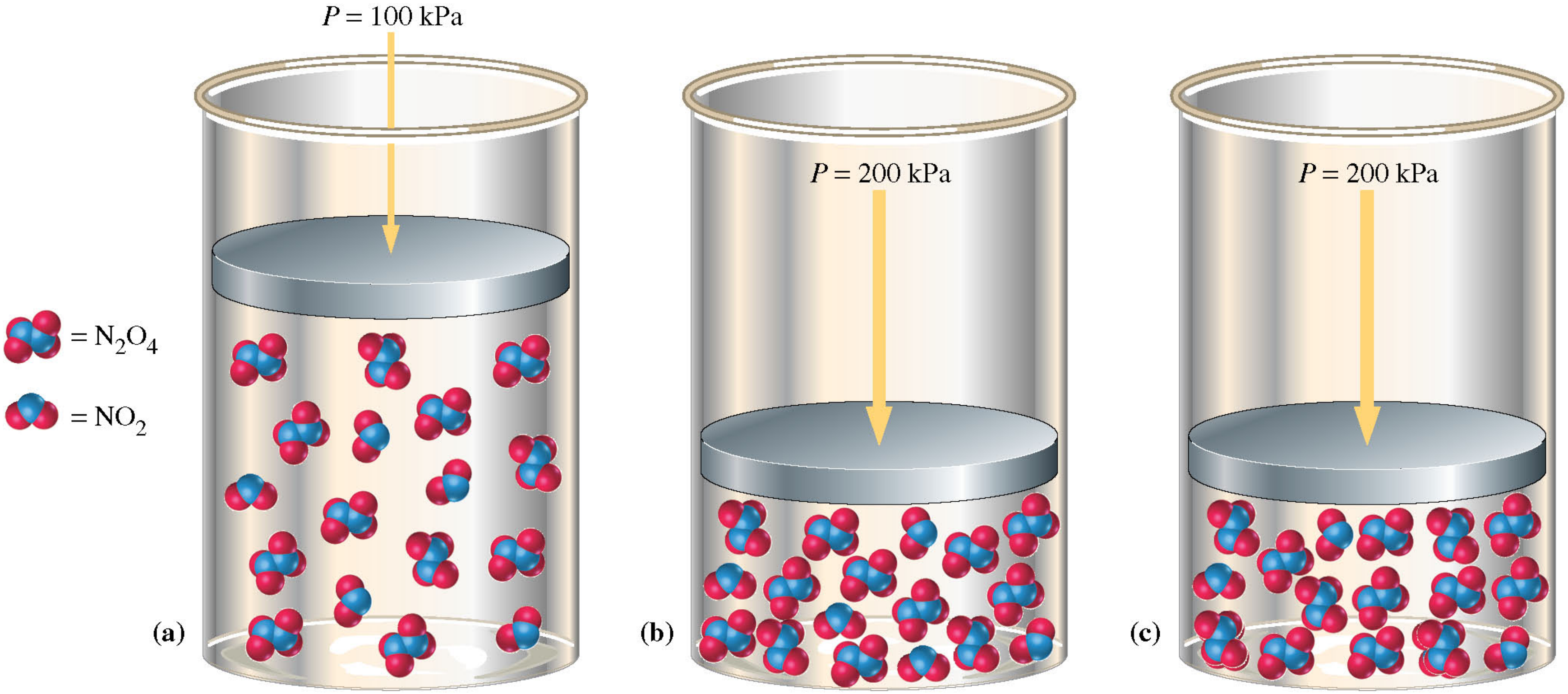
If we increase the concentration of a reactant:

the equilibrium is shifted towards products

If we increase the concentration of a product:

the equilibrium is shifted towards reactants

2. Modifying Pressure and Volume



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

2. Modifying Pressure and Volume

$$\text{x mol of gas} \rightleftharpoons \text{y mol of gas}$$

where x > y

If the pressure is increased:

the equilibrium shifts to the « y » side

If the pressure is decreased:

the equilibrium shifts to the « x » side

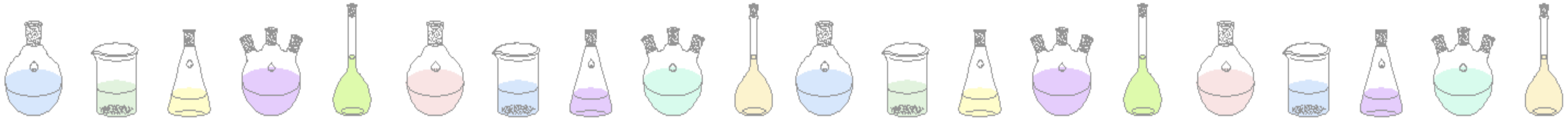
3. Modifying Temperature

- changing concentrations or pressure has no effect on the value of K
- however, the value of K is temperature-dependent
  - for an endothermic reaction, heat is a “**reactant**”

$$\mathrm{A} + \mathrm{heat} \leftrightarrows \mathrm{B}$$

  - for an exothermic reaction, heat is a “**product**”

$$\mathrm{A} \leftrightarrows \mathrm{B} + \mathrm{heat}$$



3. Modifying Temperature

ENDOTHERMIC: $A + \text{heat} \leftrightarrows B$

If the temperature is increased:

the equilibrium is shifted towards products

If the temperature is decreased:

the equilibrium is shifted towards reactants

3. Modifying Temperature

EXOTHERMIC:

$$A \leftrightarrows B + \text{heat}$$

If the temperature is increased:

the equilibrium is shifted towards reactants

If the temperature is decreased:

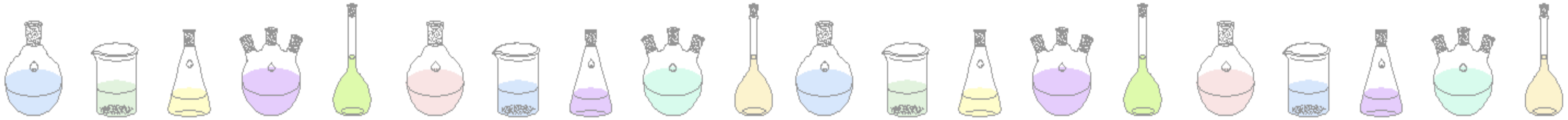
the equilibrium is shifted towards products

Your Turn…

For the following equilibrium, which would be the most effective method to encourage the **forward** reaction?

$$A\,(g) + 2\,B\,(g) \leftrightarrows C\,(g) \qquad \Delta H_{rxn} = +\,32\ \text{kJ/mol}$$

A. Add C + add heat
B. Remove B + add heat
C. Add B + remove heat
D. Decrease volume, add heat
E. Add A + increase volume
F. I’m not sure



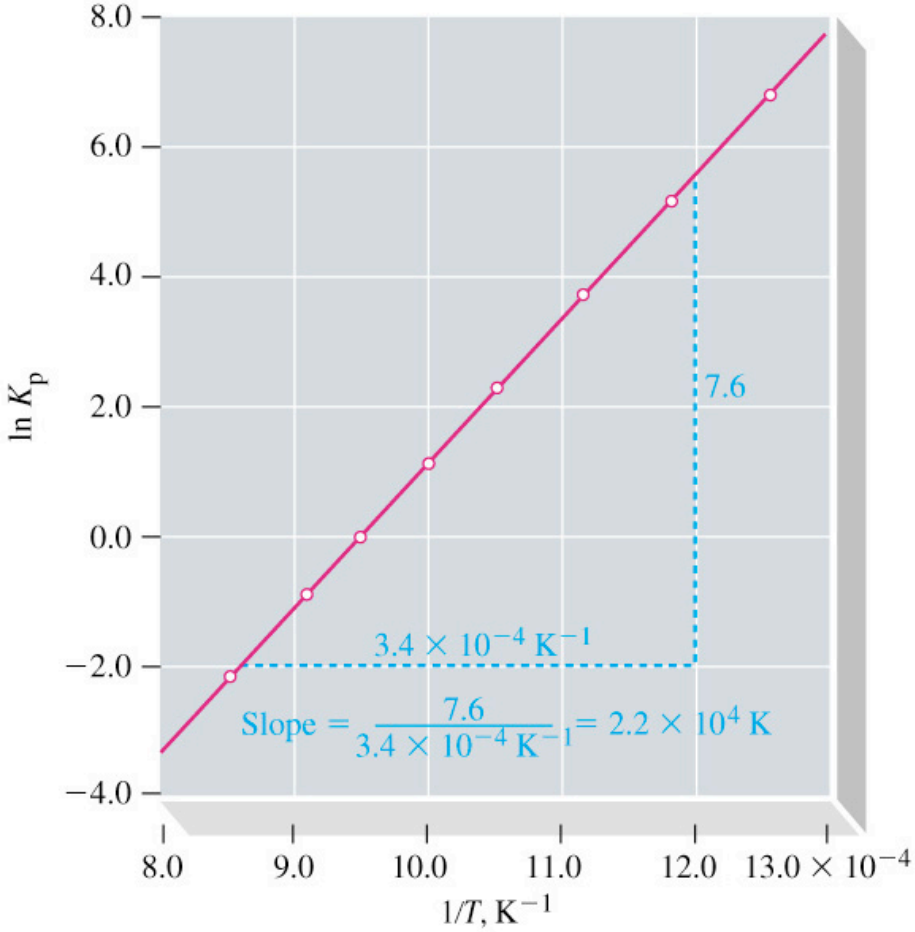
Temperature Dependence of K

For graphs of $\ln K_{eq}$ versus 1/T:

$$\ln K_{eq} = -\frac{\Delta H^o}{R} \bullet \frac{1}{T} + \frac{\Delta S^o}{R}$$

slope =

y-intercept =



The van’t Hoff Equation

- two different equilibrium constants (K_1 and K_2) at two different temperatures (T_1 and T_2):

$$\ln K_1 = -\frac{\Delta H^o}{R} \bullet \frac{1}{T_1} + \frac{\Delta S^o}{R}$$

$$\ln K_2 = -\frac{\Delta H^o}{R} \bullet \frac{1}{T_2} + \frac{\Delta S^o}{R}$$

$$\boxed{\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

The van’t Hoff Equation

Don’t confuse k and K!

EQUILIBRIUM

van’t Hoff Equation:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Graph of ln K vs. 1/T:

slope = $-\Delta H^o/R$

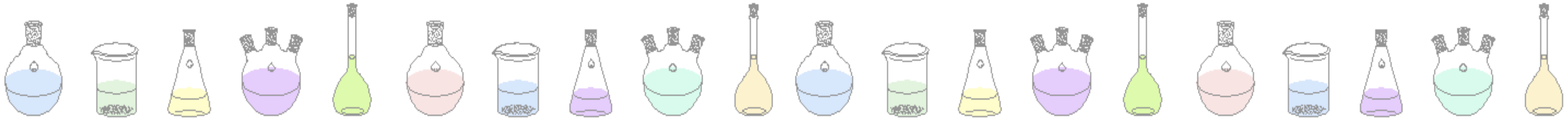
KINETICS

Arrhenius Equation:

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

Graph of ln k vs. 1/T:

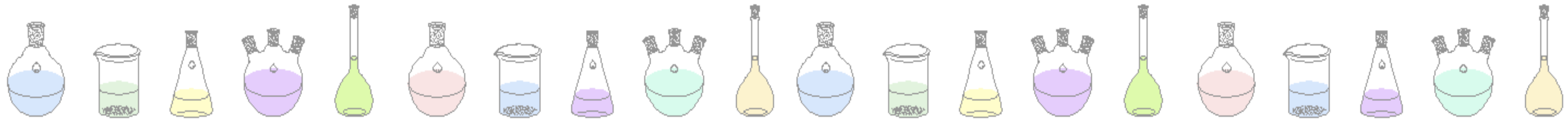
slope = $-E_a/R$



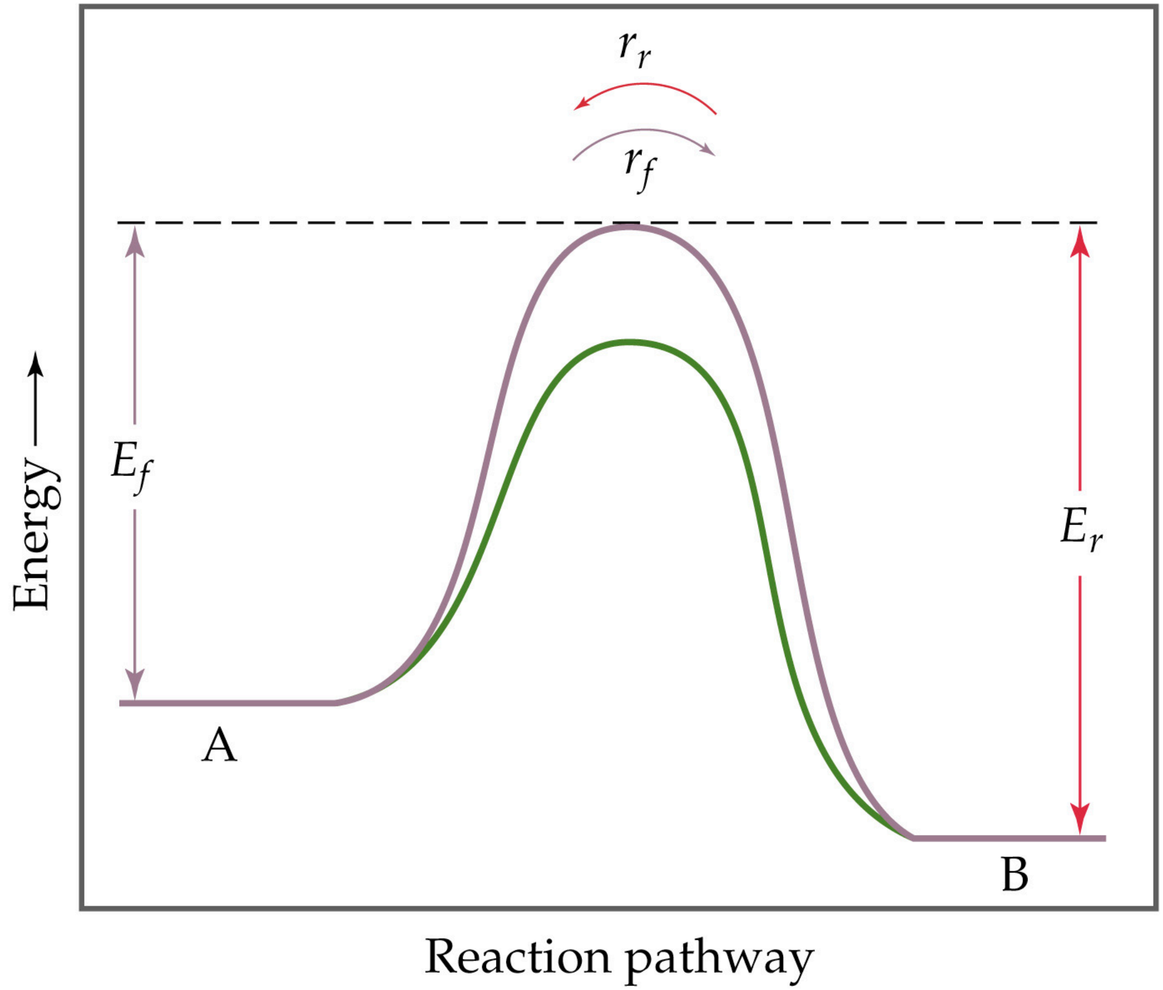
4. Adding a Catalyst

The Effect of Catalysis

- A catalyst lowers the activation energy barrier for the reaction.
- Therefore, a catalyst will decrease the time taken to reach equilibrium.
- A catalyst does not effect the composition of the equilibrium mixture.

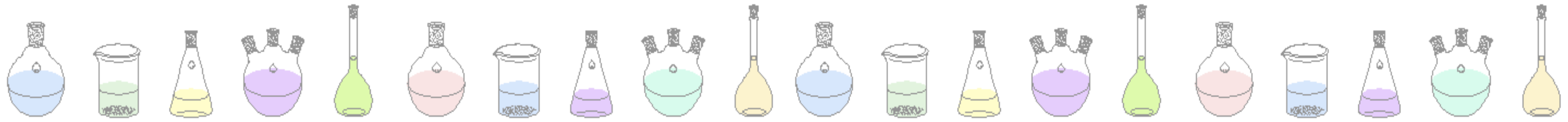


Adding a catalyst



Chapter 15 Key Concepts

1. Dynamic Equilibrium
2. Equilibrium Constant Expression, K
3. Manipulating K values
4. The Reaction Quotient, Q
5. Le Châtelier’s Principle
6. van’t Hoff Equation
7. Equilibrium Problems and ICE Tables



Suggested Chapter 15 Problems

15.1, 15.7, 15.12, 15.16, 15.23, 15.29, 15.31, 15.35, 15.38, 15.41, 15.45, 15.47, 15.53, 15.55, 15.59, 15.63, 15.69, 15.73, 15.81, 15.87, 15.95, 15.97, 15.99, 15.103, 15.109