Chemical Equilibrium

CHM 101

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Chemical Equilibrium

- When some types of chemical reactions occur in the gas or solution phases, these reaction attain "chemical equilibrium", *i.e.*, the reaction does not go to completion, but the reaction vessel will contain both reactant species and product species mixed together.

Chemical Equilibrium

- This occurs when the concentrations of the reactants stop decreasing, and the concentrations of the products stop increasing. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

$$2\ NO_2 \leftrightarrow N_2O_4$$

(I will use $\leftrightarrow$ to indicate an equilibrium process in my lecture notes)

Chemical Equilibrium

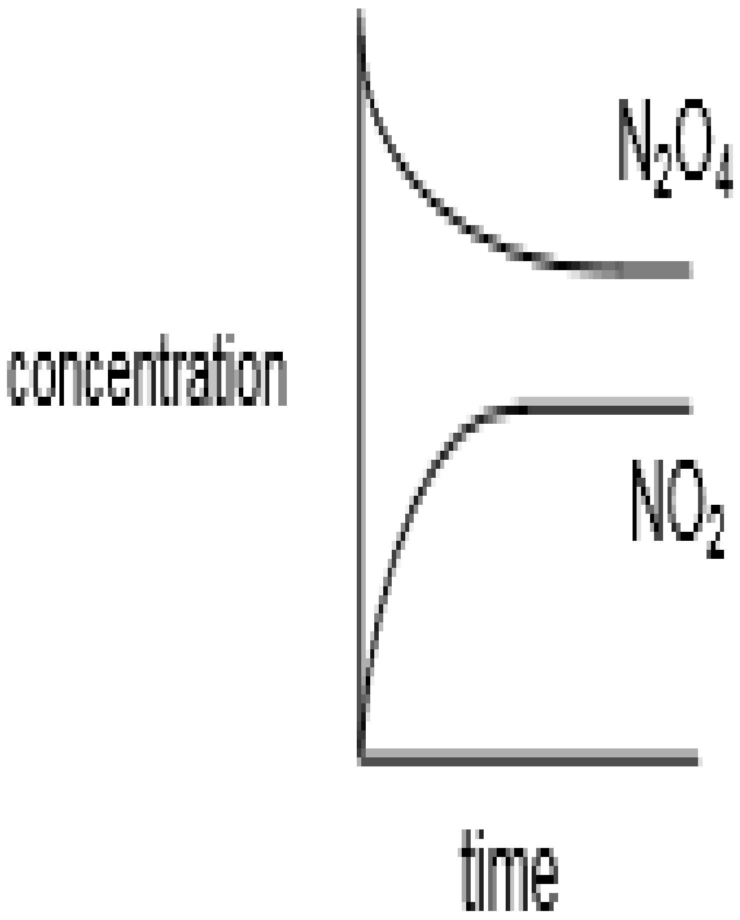
Many chemical reactions do not go to completion but instead attain a state of chemical equilibrium.

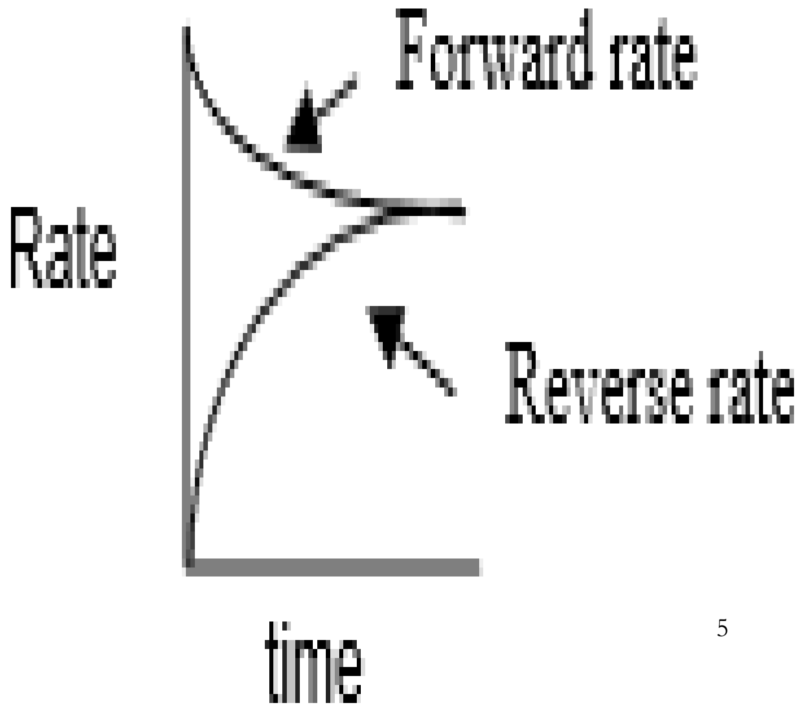
Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

⇒ Equilibrium is a dynamic process the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules. For the reaction: $N_2O_4(g) \leftrightarrow 2NO_2(g)$

Chemical Equilibrium

For the reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$





Chemical Equilibrium

- At any given time in a container of NO_2, some fraction of the gas will be in the form of NO_2, and some fraction will be in the form of N_2O_4.
- NO_2 is a brown gas while N_2O_4 is colorless

$$2\ NO_2 \leftrightarrow N_2O_4 \qquad N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

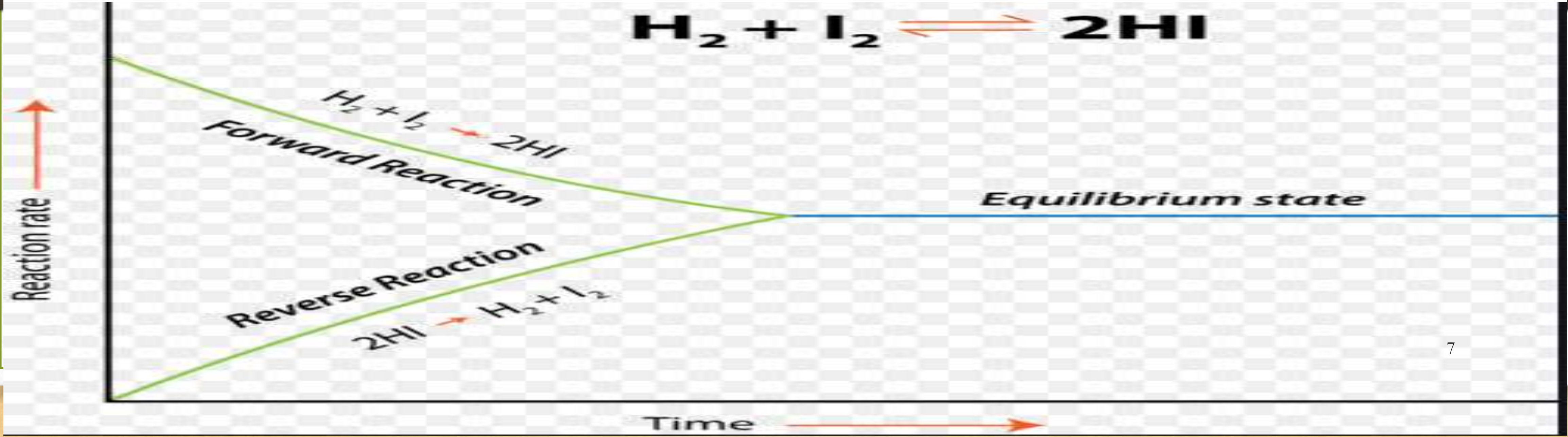
Chemical Equilibrium

Hydrogen and iodine gases react to form hydrogen iodide according to the following reaction:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

$$\text{Forward reaction: } H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$$

$$\text{Reverse reaction: } 2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$



Chemical Equilibrium

- Initially, only the forward reaction occurs because no HI is present.
- As soon as some HI has formed, it begins to decompose back into H_2 and I_2.
- Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2.
- When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance.
- **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the

Chemical Equilibrium

- At any given time in a container of NO_2, some fraction of the gas will be in the form of NO_2, and some fraction will be in the form of N_2O_4.
- Chemical equilibrium is a dynamic process—an individual molecule will repeatedly move from the NO_2 form to the N_2O_4 form, the overall concentrations of NO_2 and N_2O_4 do not change at a given temperature

$$2\ NO_2 \leftrightarrow N_2O_4$$

Equilibrium Constants

- The "equilibrium constant", K_{eq}, for a chemical reaction indicates whether the reactants or the products will be favored in an equilibrium process
- The equilibrium constant in terms of concentrations is defined as:

$$aA + bB \rightleftharpoons cC + dD$$

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

Equilibrium Constant

Law of mass action also forms the basis which states that the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants raised to their respective stoichiometric coefficients. Therefore, given the reaction –

$$aA(g) + bB(g) \Leftrightarrow cC(g) + dD(g)$$

- By using the law of mass action here,
  - The forward reaction rate would be $k_+ [A]^a[B]^b$
  - The backward reaction rate would be $k_- [C]^c[D]^d$

Equilibrium Constant

where, [A], [B], [C] and [D] being the active masses and k_+ and k_- are rate constants of forward and backward reactions, also the a, b, c, d are the stoichiometric coefficients related to A, B, C and D respectively. However, at the equilibrium – the forward and the backward rates are equal, stating –

Rate of forward reaction = Rate of backward reaction

$$K_f[A]^a[B]^b = K_b[C]^c[D]^d$$

Equilibrium Constant

or,

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

or,

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

Equilibrium Constant

where,

$$K_c = \frac{K_f}{K_b}$$

K_c is the equilibrium constant expressed in terms of the molar concentrations. The equation $K_c = [\,C\,]^c.[\,D\,]^d \,/\, [\,A\,]^a.[\,B\,]^b$

Law of mass action - The value of the equilibrium constant expression, Kc, is constant for a given reaction at equilibrium and at a constant temperature.

⇒ The equilibrium concentrations of reactants and products may vary, but the value for Kc remains the same.

The Equilibrium Constant

For a reaction: $aA + bB \rightleftharpoons cC + dD$

equilibrium constant: $$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Equilibrium Constant

The Equilibrium Constant

For a reaction: $aA + bB \rightleftharpoons cC + dD$

equilibrium constant: $$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The **equilibrium constant**, K_c, is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

Example. Write the equilibrium constant, K_c, for $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Equilibrium Constant

- For the $2\ NO_2 \leftrightarrow N_2O_4$ reaction, the equilibrium constant is given as:

$$K_C = \frac{[N_2O_4]}{[NO_2]^2}$$

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

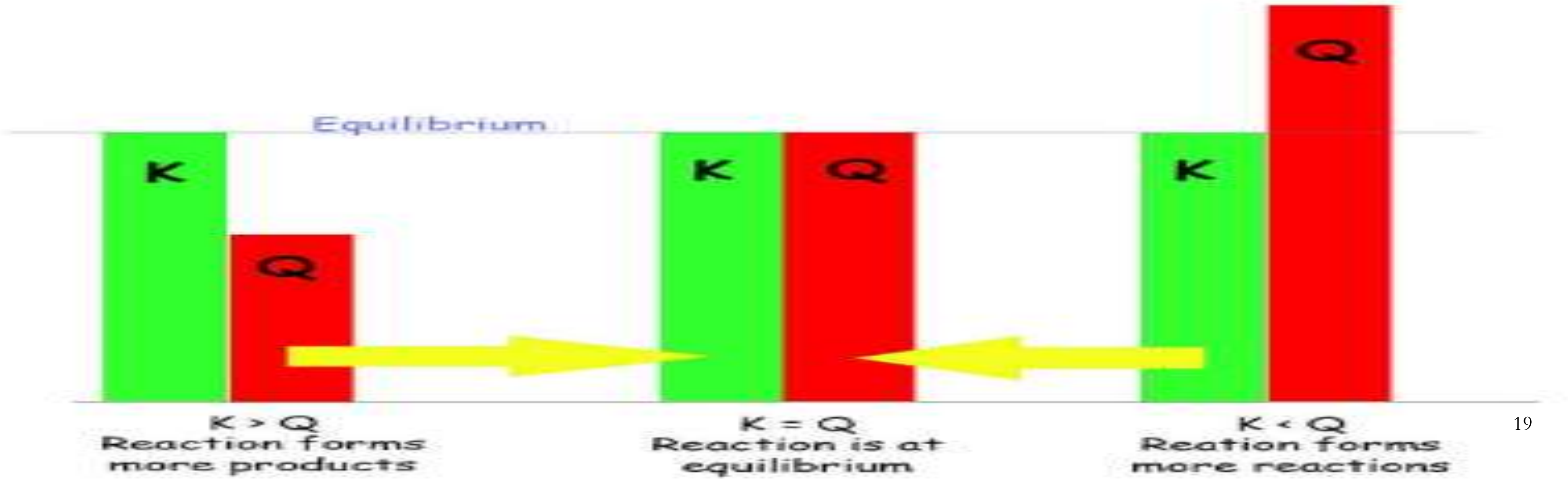
Reaction Quotient

The reaction quotient, Q, is used when questioning if we are at equilibrium. The calculation for Q is **exactly** the same as for KK but we can only use K when we know we are at equilibrium. Comparing Q and K allows the direction of the reaction to be predicted.

- $Q = K$ equilibrium
- $Q < K$ reaction proceeds to the right to form more products and decrease amount of reactants so value of Q will increase.
- $Q > K$ reaction proceeds to the left to form more reactants and decrease amount of products so value of Q will decrease.

How the Gas Equilibrium Constants Relate to Reaction Quotient (Q)

The process of finding the Reaction Quotient (Q_c) is the same as finding K_c and K_p, where the products of the reaction is divided by the reactants of the reaction (Products/Reactants) <u>at any time not necessarily at equilibrium</u>.



Equilibrium Constant

The **equilibrium constant, K_c,** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

Example. Write the equilibrium constant, K_c, for $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Other Characteristics of K_c

1) Equilibrium can be approached from either direction.
2) K_c does not depend on the initial concentrations of reactants and products.
3) K_c does depend on temperature.

Magnitude of K_c

⇒ If the K_c value is large ($K_c >> 1$), the equilibrium lies to the right and the reaction mixture contains mostly products.

⇒ If the K_c value is small ($K_c << 1$), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

⇒ If the K_c value is close to 1 ($0.10 < K_c < 10$), the mixture contains appreciable amounts of both reactants and products.

WHAT DOES THE EQUILIBRIUM CONSTANT TELL US?

If a problem asks you to find which way the reaction will shift in order to achieve equilibrium, and K is *given*, you would have to calculate for Q and compare the two numbers.

When comparing K and Q:

- $K < Q$: Since there are more products than reactants, the reaction will produce more reactants to reach equilibrium, the reaction favors the reactants.
- $K > Q$: Since there are more reactants than products, the reaction will produce more products to reach equilibrium, the reaction favors the products.
- $K = Q$: There is no change in the products nor reactants, so equilibrium is achieved.

WHAT DOES THE EQUILIBRIUM CONSTANT TELL US?

Predicting the Direction of Reaction

- The reaction quotient, Q, is the resulting value when we substitute reactant and product concentrations into the equilibrium expression.

1. If Q > K, the reaction will go to the left.
   - The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.
2. If Q < K, the reaction will go to the right.
   - The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.
3. If Q = K, the reaction mixture is already at equilibrium, so no shift occurs.

How the Gas Equilibrium Constants Relate to Reaction Quotient (Q)

A trick to remember to which what the reaction will favor is:

Put: K _ Q (in alphabetical order! - or it will not work)

$K < Q$: K ←← Q

The reaction will favor the reactants because reactants are on the left of the equation. $K > Q$: K →→ Q

The reaction will favor the products because products are on the right of the equation. $K = Q$: NO CHANGE

Work Out Example

- Example. For the reaction, B 2A, Kc = 2. Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask.

(a) In which direction will the reaction proceed to attain equilibrium?

(b) Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

Solution:

WRITING EQUILIBRIUM CONSTANT EXPRESSIONS

- Calculating Equilibrium Constants, Kc
- Kc values are listed without units ⇒ don't include units when calculating Kc.
- If equilibrium concentrations are known, simply substitute the concentrations into the equilibrium constant expression:
- Example.
- For the reaction, $CO + 3H_2 \leftrightarrow CH_4 + H_2O$,
- Calculate Kc from the following equilibrium concentrations:

Homogeneous & Heteroenous Equilibria

- Homogeneous equilibria: reactants and products exist in a single phase.
- For the gas phase reaction:

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

- The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, Kc, is:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Homogeneous & Heteroenous Equilibria

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

Homogeneous equilibria: reactants and products exist in a single phase.

For the gas phase reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

The equilibrium constant with the concentrations of reactants and products expressed in terms of molarity, K_c, is:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

Heterogeneous Equilibria and Solvents in Homogeneous Equilibria

- Heterogeneous equilibria: reactants and products are present in more than one phase.
- ~~pure solids and liquids: concentrations of pure solids and liquids are fixed~~ by their density and molar mass (both constants) and do not vary with the amount.

$$[\ ] = M = \frac{Density}{Molar\ Mass} \qquad M = \frac{mol}{L} = \frac{g}{ml} \times \frac{10^3\ ml}{1L} \times \frac{mol}{g}$$

Thus, the concentrations of solids and liquids are incorporated in the Kc value; they are not part of the variable Kc expression:

Homogeneous & Hetroenou Equilibria

- If the reaction involves a pure solid or pure liquid, these species do not appear in the equilibrium constant expression:

<u>Example:</u>

$$CH_4(g) + H_2O(\ell) \leftrightarrow CO(g) + 3\,H_2(g)$$

$$K_C = \frac{[CO(g)]\,[H_2(g)]^3}{[CH_4(g)]}$$

Note that $H_2O(\ell)$ does not appear in the denominator.

Heterogeneous equilibria

Omit concentration terms for solids and liquids from Kc and Kp expressions; only include terms for gases (g) and aqueous substances (aq).

Example. Write the K_c expression for $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$$3Cu_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+{}_{(aq)} \rightleftharpoons 3Cu^{2+}{}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$$

Example. For N2(g) + 3H2(g) 2NH3(g), does the equilibrium shift left or right if the pressure is increased?

E.g. For $H_2 + I_2 \rightleftharpoons 2HI$,

For $H_2 + I_2 \rightleftharpoons 2HI$,

For $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$,

Gas Phase Expressions can also be expressed by Kp

⇒ The Kp expression is written using equilibrium partial pressures of reactants & products. For the reaction given above, the Kp expression is:

$$K_p = \frac{P_{NO_2}^{\ 2}}{P_{N_2O_4}}$$

Worked out Examples: For: H2 + I2 ↔ 2HI, does the equilibria shift left or right if we: a) add H2? b) remove I2?

a)

b)

finding Kp, from partial pressures

- **Example 1: finding *K*p, from partial pressures**
- Let's try finding *K*p, for the following gas-phase reaction:

$$2N_2O_5(g) \leftrightharpoons O_2(g) + 4NO_2(g)$$

We know the partial pressure for each component at equilibrium for some temperature T, Given that P_{N2O5} = 2.00 atm, P_{O2} = 0.296 atm, P_{NO2} = 1.70 atm. A temperature T, what is K_p for the reaction?

<u>Solution</u>: **At temperature T, what is *K*p, for this reaction?**

First we can write the *K*p expression for our balanced equation:

We can now solve for *K*p, by plugging in the equilibrium partial pressures in the equilibrium expression:

$$K_p = \frac{(P_{O_2})(P_{NO_2})^4}{(P_{N_2O_5})^2}$$

$$K_p = \frac{(0.296)(1.70)^4}{(2.00)^2} = 0.618$$

Kp is related to Kc

- Since pressure and molarity are related by the Ideal Gas Law, the following equation relates Kp and Kc:

$$K_p = K_c(RT)^{\Delta n}$$

where $R = 0.0821 \dfrac{L \cdot atm}{K \cdot mol}$; T = temperature in Kelvin

Δn = moles of gaseous products – moles of gaseous reactants

⇒ Note that Kc = Kp when the number of gas molecules are the same on both sides.

Kc and Kp

$$aA + bB \rightleftharpoons cC + dD$$

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

$$K_p = \frac{(C)^c(D)^d}{(A)^a(B)^b}$$

Consider an example

$2A_{(g)} + B_{(g)} \leftrightharpoons 2C_{(g)}$ All in the gas phase.

The K_p is given by-

$$K_P = \frac{P_C^2}{P_A^2 P_B} \text{———} (1)$$

Ideal Gas Equation

Each of these ideal gas molecules behaves similarly. So for each of them,

PV = nRT

On rearranging we get-

$$P = \frac{n}{V} RT$$

Substituting these in equation (1)

$$P = \frac{n}{V}RT$$

$$\Rightarrow K_p = \frac{[C]^2(RT)^2}{[A]^2(RT)^2[B](RT)} \Rightarrow K_p = \frac{[C]^2}{[A]^2[B]} \times \frac{(RT)^2}{(RT)^2(RT)}$$

On canceling like terms and substituting $K_c = \frac{[C]^2}{[A]^2[B]}$ we get-

$$\Rightarrow K_p = \frac{K_c}{RT}$$

Or

$$K_p = K_c(RT)^{-1}$$

In general,

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = K_p(RT)^{-\Delta n}$$

- Where, Δn represents the change in the number of moles of gas molecules. [That is Δn = product – reactant in moles only for gas molecules]
- **When the change in the number of moles of gas molecules is zero, that is $\Delta n = 0$**

$$\Rightarrow K_p = K_c$$

In general, for any chemical reactions of gas molecules relation between K_p And K_c is-

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = K_p(RT)^{-\Delta n}$$

Equilibrium Constant and Pressure

- How does the expression for the equilibrium constant change if pressure is used as the variable instead of concentration?
- Using the Ideal Gas Law:

$$P_A = \frac{nRT}{V} = [A]RT$$

$$\therefore [A] = \frac{P_A}{RT}$$

Example 2: finding Kp, from Kc.

- Now let's look at a different reversible reaction:

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

If K_c for this reaction is 4.5×10^4 at $400\,K$, what is the equilibrium constant, K_p, at the same temperature?

$$\Delta n = \text{mol of product gas} - \text{mol of reactant gas}$$

$$= 2\,\text{mol}\,NH_3 - (1\,\text{mol}\,N_2 + 3\,\text{mol}\,H_2)$$

$$= -2\,\text{mol gas}$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = K_c(RT)^{\Delta n}$$

$$= (4.5 \times 10^4)(R \cdot 400)^{-2}$$

$$= (4.5 \times 10^4)(0.08314 \cdot 400)^{-2}$$

$$= 41$$

will use $R = 0.08314 \dfrac{L \cdot bar}{K \cdot mol}$.

WORKED OUT EXAMPLES

Example. Does $K_c = K_p$ for (a) $H_{2(g)} + F_{2(g)} \rightleftharpoons 2HF_{(g)}$? (b) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$?

Example. For the reaction, $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ (a) write the equilibrium constant expression, K_p. (b) What is the value for K_p if $K_c = 2.8\times10^2$ at 1000 K?

Le Chatelier's Principle

- Le Chatelier's principle states that if a **dynamic equilibrium** is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium.
- If a chemical reaction is at equilibrium and experiences a change in pressure, temperature, or concentration of products or reactants, the equilibrium shifts in the opposite direction to offset the change.
- This page covers changes to the position of equilibrium due to such changes and discusses briefly why catalysts have no effect on the equilibrium position.

Recall factors that Le Chatelier's principle states will affect the equilibrium of a system

- **Key Points**

Le Chatelier's principle can be used to predict the behavior of a system due to changes in pressure, temperature, or concentration.

- Le Chatelier's principle implies that the addition of heat to a reaction will favor the endothermic direction of a reaction as this reduces the amount of heat produced in the system.
- Increasing the concentration of reactants will drive the reaction to the right, while increasing the concentration of products will drive the reaction to the left.

Changes in Volume and Pressure

- Because the pressure of gases is related directly to the concentration by P = n/V,

changing the pressure by increasing/decreasing the volume of a container will disturb an equilibrium system.

⇒ If P increases (V decreases), the system shifts to the side with a smaller number of gas molecules (this effectively reestablishes equilibrium by decreasing the pressure).

⇒ If P decreases (V increases), the system shifts to the side with a greater number of gas molecules.

Changes in Temperature

- Heat can be considered a reactant in an endothermic rxn and a product in an exothermic rxn. Heat can be considered a reactant in an endothermic rxn and a product in an exothermic rxn.

For $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$,

Endothermic ($\Delta H > 0$)	$R + Heat \rightleftharpoons Products$
Exothermic ($\Delta H < 0$)	$R \rightleftharpoons Products + Heat$

Changes in Temperature

- K_c is larger when the reaction shifts right. This occurs if T is increased for an Endothermic Reaction or T is decreased for an Exothermic reaction.
- K_c is smaller when the reaction shifts left. This occurs if T is decreased for an Endothermic Reaction or T is increased for an Exothermic reaction.

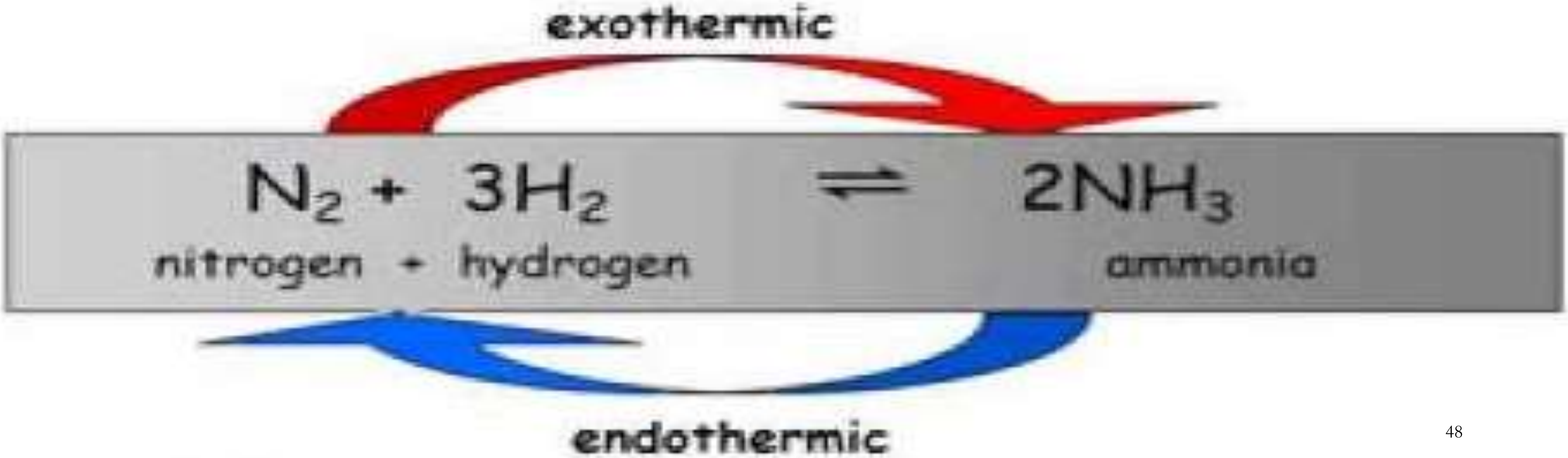
Example. If the temperature is decreased for the reaction: $2CO_2 \rightleftharpoons 2CO + O_2$, $\Delta H = 566$ kJ.

a) Will the equilibrium shift left or right? b) Does K_c become larger or smaller?

Energy Changes in reversible reactions

Reversible reactions are exothermic (give out heat) in one direction and endothermic (take in heat) in the other.

The same amount (Joules) of heat energy is given out in one direction and taken in in the other direction.



Changes in concentration

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

← Equilibrium shifts to left (reactants side)

Adding HI - equilibrium shifts to the left to 'use up' added HI (K_c doesn't change).

Le Châtelier's Principle Summary

Variable	Type of Change	Response of System
concentration	increase	shifts to consume some of the added reactant or product
	decrease	shifts to replace some of the removed reactant or product
temperature	increase	shifts to consume some of the added thermal energy
	decrease	shifts to replace some of the removed thermal energy
volume	increase (decrease in pressure)	shifts toward the side with the larger total amount of gaseous entities
	decrease (increase in pressure)	shifts toward the side with the smaller total amount of gaseous entities
Variables That Do Not Affect Chemical Equilibria		
catalysts	–	no effect
inert gases	–	no effect

Le Chatelier's Principle and Chemical Equlibrium

- When changing temperature is the applied stress, the exothermic or endothermic nature of the reaction must be considered.
- When heat is added to endothermic reactions they shift forward. When heat is removed from endothermic reactions they shift in reverse.
- When heat is added to an exothermic reactions they shift reverse. When heat is removed from exothermic reactions they shift forward.
- Endothermic reactions are identified with a positive ΔH or heat written into the equation as a reactant. Exothermic reactions are identified with a negative ΔH or heat written into the equation as a product.

Effect of a Catalyst

- Choosing Optimum Conditions
- Le Chateliers principle can be used to select optimum conditions to form a substance. e.g. To form more NH3, predict the optimum conditions for temperature and pressure.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -91.8\ kJ$$

Example 1: Thermal Decomposition of $NH_4SH_{(s)}$NH4SH(s)

This also is related to K_{sp}

$$aA + bB \rightleftharpoons cC + dD$$

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

$$K_p = \frac{(C)^c(D)^d}{(A)^a(B)^b}$$

$$NH_4SH_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

$$K_c = \frac{[NH_3][H_2S]}{[NH_4SH]}$$

$$K_c = \frac{[NH_3][H_2S]}{[1]}$$

$$K_c = [NH_3][H_2S]$$

$$K_c = \frac{[NH_3][H_2S]}{[1]}$$

$$K_c = [NH_3][H_2S]$$

$$K_p = \frac{(NH_3)(H_2S)}{(NH_4SH)}$$

$$K_p = \frac{(NH_3)(H_2S)}{(1)}$$

$$K_p = (NH_3)(H_2S)$$

$$K_c = \frac{[NH_3][H_2S]}{[1]}$$

$$K_c = [NH_3][H_2S]$$

but since NH_4SHNH4SH is a solid, we get:

Example 2: Hydrogen and Iodine

Consider the double replacement reaction of hydrogen and iodine gas:

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

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

$$K_p = \frac{(HI)^2}{(H_2)(I_2)}$$

Example 3

Given: NOBr= 0.46 M

NO= 0.1 M

Br_2 = 0.3M

To set up K_c, it is $\dfrac{Products}{Reactants}$

$$K_c = \dfrac{[NO]^2 \; [Br_{2}]}{[NOBr]^2}$$

$$K_c = \dfrac{[0.1]^2 \; [0.3]}{[0.46]^2}$$

$$2NOBr_{(g)} \rightleftharpoons 2NO_{(s)} + Br_{2(g)}$$

Answer: K_c= 0.0142 M