Chapter 6: Chemical Equilibrium

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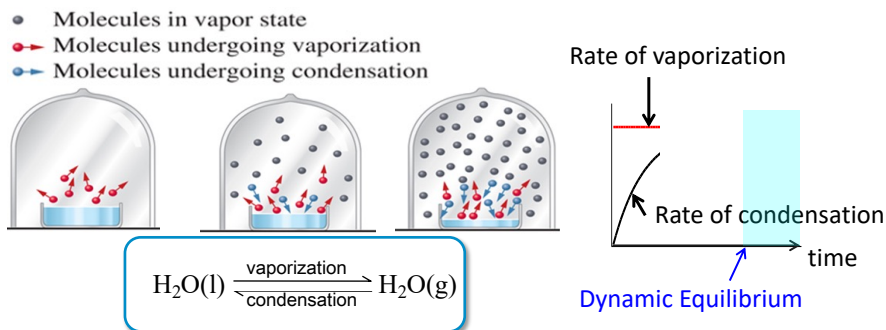The Reaction Quotient A: Predicting the Direction of Net Change

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Vapor Pressure of Liquids

- Molecules in vapor state
- Molecules undergoing vaporization
- Molecules undergoing condensation

Rate of vaporization

Rate of condensation

time

Dynamic Equilibrium

$$H_2O(l) \xrightarrow[\text{condensation}]{\text{vaporization}} H_2O(g)$$

When the beaker with sufficient water is placed in a closed container, the **dynamic equilibrium** will be established when the **rate of vaporization** equals the **rate of condensation**.

Vapor pressure is the pressure of a vapor in a dynamic equilibrium with its condensed phase.

Vapor pressure **depends only on temperature**.
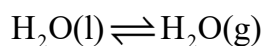
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Dynamic Equilibrium

Chemical reactions reach a state of **dynamic equilibrium** when:

- (Rate of forward reaction) = (Rate of reverse reaction)
- There is no net change in composition.

e.g. A water vaporizes within a closed container. The rate of condensation is equal to the rate of vaporization once the partial pressure of water reaches the water vapor pressure.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

Forward reaction: $H_2O(l) \rightarrow H_2O(g)$

Reverse reaction: $H_2O(g) \rightarrow H_2O(l)$
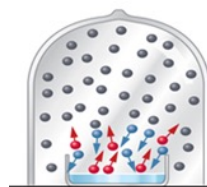
If a reaction mix starts out or is forced away from equilibrium, the composition will change until equilibrium is established.
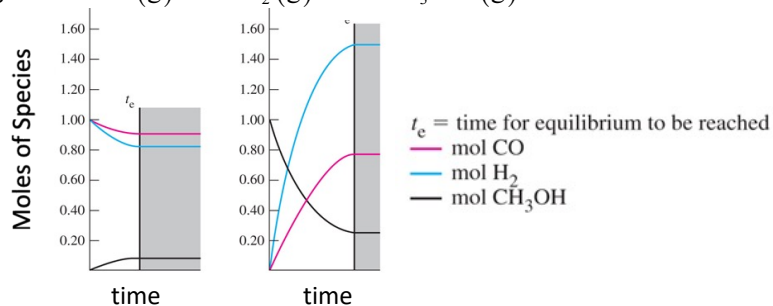
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Initial Conditions and Equilibria

Different initial conditions may lead to different equilibria.

e.g. $CO\,(g)\ +\ 2\,H_2\,(g)\ \rightleftharpoons\ CH_3OH\,(g)$ at V=1L

t_e = time for equilibrium to be reached
— mol CO
— mol H_2
— mol CH_3OH

However, the following <u>ratio of equilibrium molar concentrations</u> always gives a constant value for a given temperature. The constant is called **equilibrium constant**.
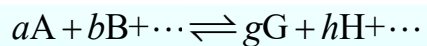
$$\frac{[CH_3OH]_{eq}}{[CO]_{eq}[H_2]^2_{eq}} = \frac{0.09}{0.91 \times 0.82^2} = \frac{0.22}{0.78 \times 1.56^2} = 0.15 = K_c$$

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Equilibrium Constant Expression

Consider a general chemical equation:

$$aA + bB + \cdots \rightleftharpoons gG + hH + \cdots$$

Here, A,B,$\cdots$ are reactants, $a,b,$ $\cdots$ are their coefficients,
G,H, $\cdots$ are products, and $g,h,$ $\cdots$ are their coefficients.

The **equilibrium constant K_c** provides the general description of the equilibrium condition and is given by:

$$K_c = \frac{[G]^g[H]^h \cdots}{[A]^a[B]^b \cdots}$$

Products ⟵ (top)
Reactants ⟵ (bottom)

The square brackets indicate the **molarity at equilibrium**.

The molarities of reactants and products must be written <u>without unit</u>, and therefore <u>K_c is unitless</u>.

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Example 6-1: Equilibrium Constant

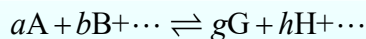For the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, $K_c = 92.0$

When equilibrium concentrations of HI and I_2 are [HI] = 0.115 M and [I_2] = 0.250 M, calculate the equilibrium concentration of [H_2].

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Equilibria involving Gases

For gaseous equilibria, you can also define the equilibrium constant in terms of the partial pressures, in atm, of reactants and products.

$$a\mathrm{A}+b\mathrm{B}+\cdots \rightleftharpoons g\mathrm{G}+h\mathrm{H}+\cdots$$

$$K_p \equiv \frac{P_\mathrm{G}^{\,g}\,P_\mathrm{H}^{\,h}\cdots}{P_\mathrm{A}^{\,a}\,P_\mathrm{B}^{\,b}\cdots}$$

The Two equilibrium constants K_c and K_p are related as:

$$K_p = K_c (RT)^{\Delta n_{gas}}$$ Here $\Delta n_{gas} = (g+h+\cdots)-(a+b+\cdots)$

Δn_{gas} is a change in moles of gasses. The derivation is given as:

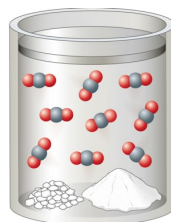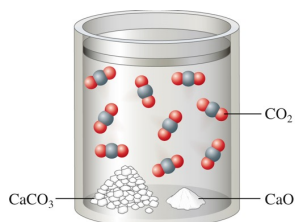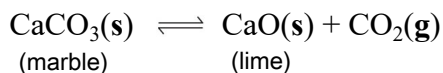$$K_c = \frac{[\mathrm{G}]^g[\mathrm{H}]^h\cdots}{[\mathrm{A}]^a[\mathrm{B}]^b\cdots} = \frac{\left(\dfrac{n_\mathrm{G}}{V}\right)^g\left(\dfrac{n_\mathrm{H}}{V}\right)^h\cdots}{\left(\dfrac{n_\mathrm{A}}{V}\right)^a\left(\dfrac{n_\mathrm{B}}{V}\right)^b\cdots} = \frac{\left(\dfrac{P_\mathrm{G}}{RT}\right)^g\left(\dfrac{P_\mathrm{H}}{RT}\right)^h\cdots}{\left(\dfrac{P_\mathrm{A}}{RT}\right)^a\left(\dfrac{P_\mathrm{B}}{RT}\right)^b\cdots}$$

$$= \frac{P_\mathrm{G}^{\,g}\,P_\mathrm{H}^{\,h}\cdots}{P_\mathrm{A}^{\,a}\,P_\mathrm{B}^{\,b}\cdots}(RT)^{(a+b+\cdots)-(g+h+\cdots)} = K_p(RT)^{(a+b+\cdots)-(g+h+\cdots)}$$

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Heterogeneous Equilibria

For a heterogeneous reaction, the equilibrium position does NOT depend on the amounts of pure solids or liquids present.

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$$
(marble)   (lime)

CaCO₃

CaO

When writing the equilibrium constant expression, do NOT include reacting species with state symbols **(s)** or **(l)**.

$$K_c = [\mathrm{CO_2}] \qquad K_P = P_\mathrm{CO} = K_c(RT)^1$$

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iClicker Example

For the reaction: $3 \text{ Fe(s)} + 4 \text{ H}_2\text{O(g)} \rightleftharpoons \text{Fe}_3\text{O}_4\text{(s)} + 4 \text{ H}_2\text{(g)}$, the correct Kc expression is:

A. $K_C = \dfrac{[\text{Fe}_3\text{O}_4][\text{H}_2]}{[\text{Fe}][\text{H}_2\text{O}]}$

B. $K_C = \dfrac{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}{[\text{Fe}]^3[\text{H}_2\text{O}]^4}$ [

C. $K_C = \dfrac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4}$

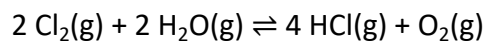D. $K_C = \dfrac{[\text{Fe}]^3[\text{H}_2\text{O}]^4}{[\text{Fe}_3\text{O}_4][\text{H}_2]^4}$

E. $K_C = \dfrac{[\text{H}_2\text{O}]^4}{[\text{H}_2]^4}$

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Example 6-2: K_p and K_c

For the following chemical equilibrium, $K_p = 4.6 \times 10^{-14}$ at 25°C, find the value of K_c for this reaction at 25° C.

    $2 \text{ Cl}_2\text{(g)} + 2 \text{ H}_2\text{O(g)} \rightleftharpoons 4 \text{ HCl(g)} + \text{O}_2\text{(g)}$
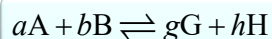
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Reaction Quotient
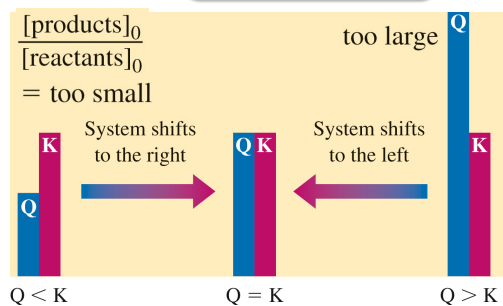
For a given initial condition, we can use the **reaction quotient** (Q) to determine the direction of a net change in establishing equilibrium.

Q_c is calculated the same way as K_C but for the **initial** concentrations ([A]$_0$, [B]$_0$, etc).

$$aA + bB \rightleftharpoons gG + hH$$

$$Q_c = \frac{[G]_0{}^g[H]_0{}^h}{[A]_0{}^a[B]_0{}^b}$$

- If $Q_c < K_c$, the reactant concentration is too high. The net reaction proceeds <u>to the right</u>.
- If $Q_c > K_c$, the product concentration is too high. The net reaction proceeds <u>to the left</u>.
- If $Q_c = K_c$, the system is at <u>equilibrium.</u> No change will occur.
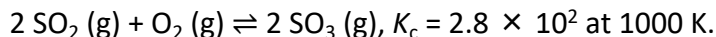
$$\frac{[products]_0}{[reactants]_0} = too\ small$$

too large

System shifts to the right

System shifts to the left

Q < K   Q = K   Q > K

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iClicker: Reaction Quotient

For the reaction

2 SO$_2$ (g) + O$_2$ (g) $\rightleftharpoons$ 2 SO$_3$ (g), K_c = 2.8 × 10^2 at 1000 K.

If a vessel is filled with these gases such that the initial concentrations are [SO$_2$] = 0.010 M, [O$_2$] = 0.070 M, and [SO$_3$] = 0.050 M, in which direction will the net reaction proceeds and why?

A. The net reaction proceeds to the right because $Q_C > K_C$.

B. The net reaction proceeds to the left because $Q_C > K_C$.

C. The net reaction proceeds to the right because $Q_C < K_C$.

D. The net reaction proceeds to the left because $Q_C < K_C$.

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Altering Equilibrium Conditions: Le Chatelier's Principle

When an 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.
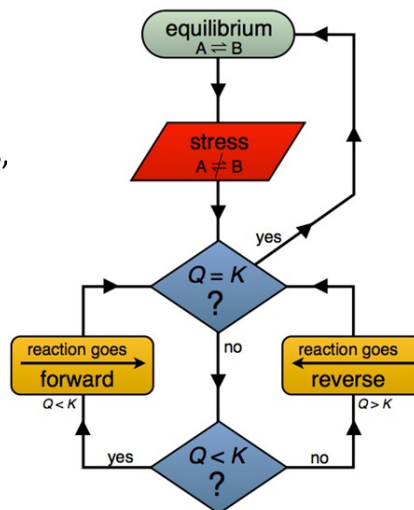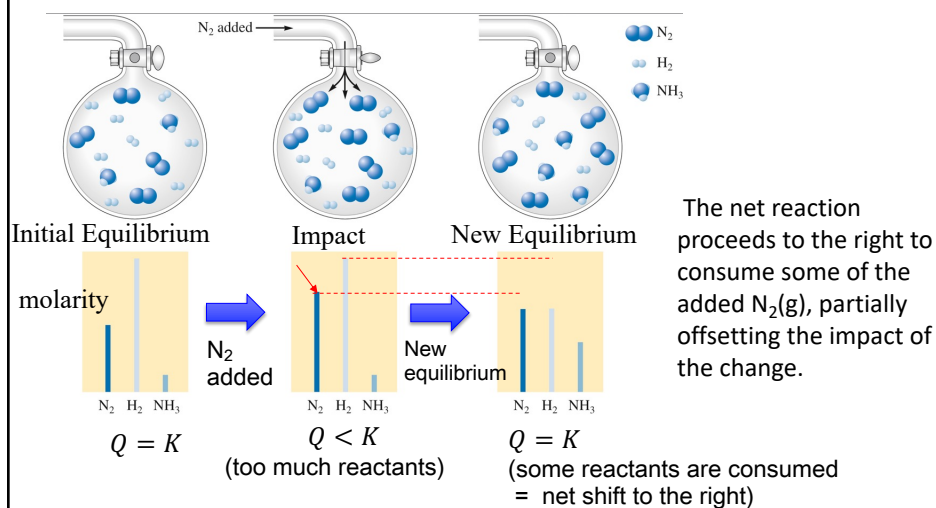
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Concentration Change

$N_2(g)$ is added to the fixed-volume system initially at equilibrium of

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

Initial Equilibrium Impact New Equilibrium

molarity

N_2 added

New equilibrium

N_2 H_2 NH_3 N_2 H_2 NH_3 N_2 H_2 NH_3

$Q = K$ $Q < K$ $Q = K$
(too much reactants) (some reactants are consumed = net shift to the right)

The net reaction proceeds to the right to consume some of the added $N_2(g)$, partially offsetting the impact of the change.
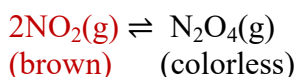
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Change in Volume

When the volume of an equilibrium mixture of gases is *reduced*, a net change occurs in the direction that produces *fewer moles of gas*.

When the volume is *increased*, a net change occurs in the direction that produces *more moles of gas*.

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

If $V \downarrow$, a net change to the right.

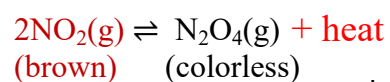© 2025 T. Hayashi, UC-Davis

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Effect of Temperature on Equilibrium

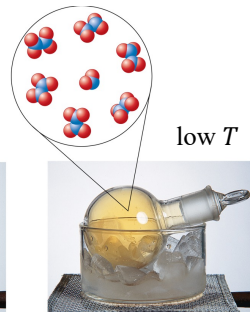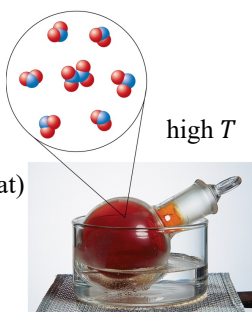Temperature does not affect Q but affects the K value.

Raising the temperature of an equilibrium mixture shifts the equilibrium in the *direction of the endothermic* reaction.

Lowering the temperature causes a shift in the *direction of the exothermic* reaction.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + heat$$
(brown)   (colorless)

$T \downarrow$
(remove heat)

high T low T

Net reaction proceeds to release heat
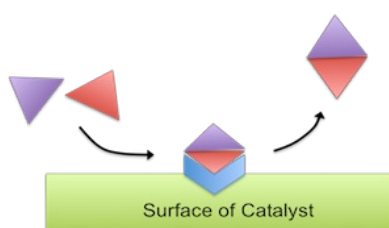
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Catalysts

A **catalyst** has **no effect** on the condition of **equilibrium** (Le Chatelier's principle does **NOT** apply). But does affect the *rate* at which equilibrium is attained.

e.g. $SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq)$
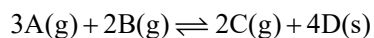The catalyst, $V_2O_5(s)$, is added
to speed up the reaction.

Surface of Catalyst

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iClicker Example: Le Chatelier's Principle

The following exothermic reaction is at equilibrium.

$$3A(g) + 2B(g) \rightleftharpoons 2C(g) + 4D(s)$$

Choose all changes (assume changes are small) which cause a shift to the right. Assume a constant volume unless specified otherwise.

A) Remove A(g)
B) Add C(g)
C) Remove D(s)
D) Decrease the volume
E) Add E(g), knowing that C(g)+E(g)→2F(g)

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ICE Tables

ICE table is a tabular system of keeping track of changing quantities in an equilibrium reaction.

e.g. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at constant V

The reaction starts with 1.00 M N_2O_4.
During the reaction to reach equilibrium, $[N_2O_4]$ decreases by x M.

ICE Table

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
Initial	1.00 M		0.0 M
Changes	$-x$ M		$+2x$ M
Equilibrium	$(1.00 - x)$ M		$2x$ M

During the change,
x M of N_2O_4 is consumed,
$2x$ M of NO_2 is formed.

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ICE Table – Equilibrium Concentrations

Given the <u>initial concentrations</u> and $\underline{K_c}$, we can calculate the equilibrium concentrations by using an ICE table.

e.g. A reaction, $A(g) + B(g) \rightleftharpoons 2C(g)$, starts with $[A]_i$ and $[B]_i$ in a constant-volume container.

	$A(g)$	$+$	$B(g)$	$\rightleftharpoons$	$2C(g)$
I	$[A]_i$ M		$[B]_i$ M		0 M
C	$-x$ M		$-x$ M		$+2x$ M
E	$[A]_i - x$ M		$[B]_i - x$ M		$2x$ M

The equilibrium constant is expressed in terms of x.

$$K_c = \frac{[C]_{eq}^2}{[A]_{eq}[B]_{eq}} = \frac{(2x)^2}{([A]_i - x)([B]_i - x)}$$

Solve the equation for x.

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Quadratic Equation

Sometimes, the equation for x is quadratic:

$$ax^2 + bx + c = 0$$

By using the following solutions of the quadratic equation, we can find two solutions:
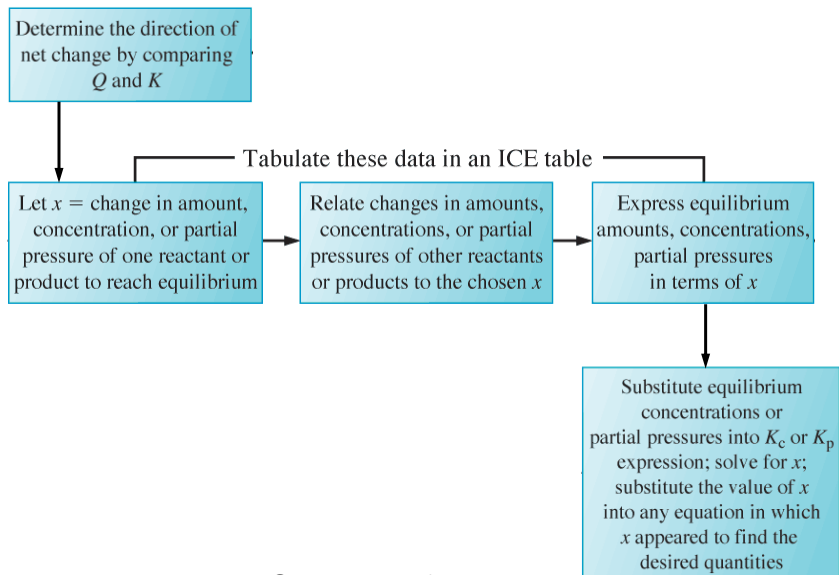
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Only **one** solution is physically meaningful. Eliminate the other.

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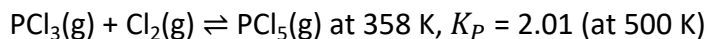## Determining Equilibrium Concentrations and Partial Pressures

Determine the direction of net change by comparing Q and K

Tabulate these data in an ICE table

Let x = change in amount, concentration, or partial pressure of one reactant or product to reach equilibrium

Relate changes in amounts, concentrations, or partial pressures of other reactants or products to the chosen x

Express equilibrium amounts, concentrations, partial pressures in terms of x

Substitute equilibrium concentrations or partial pressures into K_c or K_p expression; solve for x; substitute the value of x into any equation in which x appeared to find the desired quantities

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Example 6-4: ICE Table

Consider the reaction:

$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ at 358 K, K_P = 2.01 (at 500 K)

A mixture of 2.00 moles of PCl_3, 1.00 mole of Cl_2, and 3.00 moles of PCl_5 is introduced into a 10.0 L container and is allowed to reach equilibrium at 500 K. What are the equilibrium molar concentrations of PCl_3, Cl_2, and PCl_5?

(Hint: What is the value of K_C?)
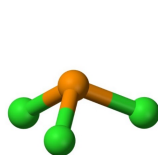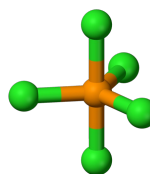
$PCl_3(g)$ $PCl_5(g)$

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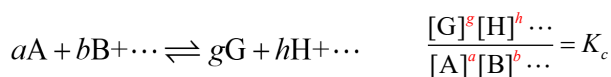
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Relationships Involving Equilibrium Constants

$$aA + bB + \cdots \rightleftharpoons gG + hH + \cdots \quad \frac{[G]^g[H]^h \cdots}{[A]^a[B]^b \cdots} = K_c$$

- Reversing the reaction causes the inversion of K.

$$gG + hH + \cdots \rightleftharpoons aA + bB + \cdots \quad \frac{[A]^a[B]^b \cdots}{[G]^g[H]^h \cdots} = \frac{1}{K_c}$$
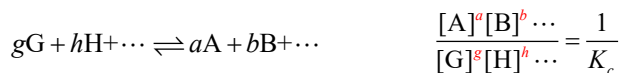
- Multiplying coefficients by a common factor x raises the equilibrium constant to the power of x.

$$xaA + xbB + \cdots \rightleftharpoons xgG + xhH + \cdots \quad \frac{[G]^{xg}[H]^{xh} \cdots}{[A]^{xa}[B]^{xb} \cdots} = \left(\frac{[G]^g[H]^h \cdots}{[A]^a[B]^b \cdots}\right)^x = K_c^x$$
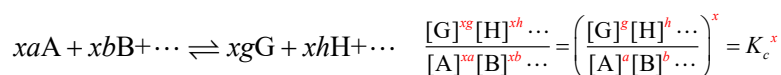
If $x = 2$, K_c^2,   If $x = 1/2$, $\sqrt{K_c}$

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Combining Equilibrium Constant Expressions

When individual chemical equations are <u>added</u>, their equilibrium constants are <u>multiplied</u> to obtain the equilibrium constant for the overall reaction.
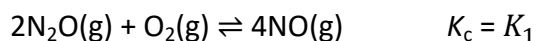
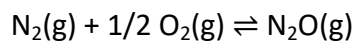Overall reaction $\quad K_c = ?$

$$aA \rightleftharpoons cC$$
$$+cC \rightleftharpoons dD$$
$$\underline{+dD \rightleftharpoons bB}$$
$$aA \rightleftharpoons bB$$

$aA \rightleftharpoons bB$; K_1 ; K_3 ; $cC \rightleftharpoons dD$; K_2

$$K_c = \frac{[B]^b}{[A]^a} = \frac{[C]^c}{[A]^a}\frac{[D]^d}{[C]^c}\frac{[B]^b}{[D]^d} = K_1 K_2 K_3$$
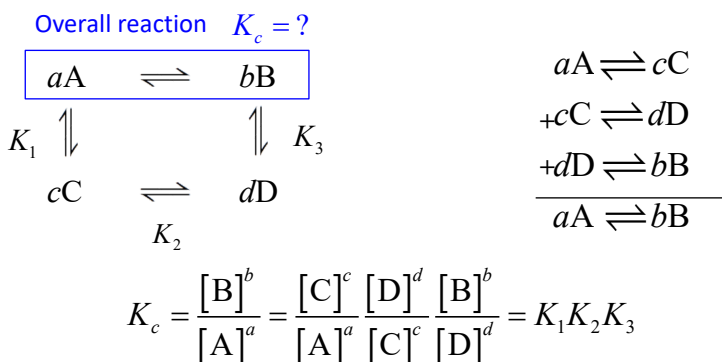
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iClicker Example: Equilibrium Constants

Given the following:

$2N_2O(g) + O_2(g) \rightleftharpoons 4NO(g) \qquad K_c = K_1$

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = K_2$

Find the expression of the equilibrium constant for the following equilibrium reaction:

$N_2(g) + 1/2\ O_2(g) \rightleftharpoons N_2O(g)$

A: $\quad K_c = \sqrt{K_1 K_2}$

B: $\quad K_c = \frac{1}{2} K_1 K_2$

C: $\quad K_c = \frac{K_2}{\sqrt{K_1}}$

D: $\quad K_c = \frac{1}{2} K_1 + K_2$

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