Chemical Equilibrium

Dr. Ron Rusay

Chemical Equilibrium

- *The reactions considered until now have had reactants react completely to form products. These reactions “went” only in one direction.*
- *Some reactions can react in either direction. They are “reversible”. When this occurs some amount of reactant(s) will always remain in the final reaction mixture.*

Chemical Equilibrium

(Definitions)

- *A chemical system where the concentrations of reactants and products remain constant over time.*
- *On the molecular level, the system is dynamic: The rate of change is the same in either the forward or reverse directions.*

Dynamic Equilibrium

“The Pennies”

- *Organize into groups of 4.*
- *Dr. R will provide your group with a number and an accounting form.*
- *In your group, select one person as:*
  - *1) Money Keeper*
  - *2) Recorder*
  - *3) Transfer Agent*
  - *4) Auditor*
- *Have the Recorder put everyone’s name on the accounting form.*
- *After recording all of the names send the Money Keeper to see Dr. R. for your capital stake.*
- *Await instructions for phase I.*

Dynamic Equilibrium

"The Pennies"

There will be 8 phases. Find your Equilibrium trading partners eg. IA with IB, IIA with IIB, etc. Below it is illustrated as1X with 1Y and 2X and 2Y.

Phase I:

Group	1 X	1 Y		2 X	2 Y
Rate	-30%	-10%		-30%	-50%
initial	40	0		20	20
change					
final					

Phase II:

initial					
change					
final					

Dynamic Equilibrium

"The Pennies"

Phase I below illustrates 1 X starting with 40 pennies and giving 12(50%) to 1 Y who has 0 pennies and has none to give 10% of; 2 X starts with 20 and gives 6(30%) to 2 Y while 2Y also starts with 20 but gives only 10(50%) to 2X.

Phase I:

Group	1 X	1 Y		2 X	2 Y
Rate	-30%	-10%		-30%	-50%
initial	40	0		20	20
change	-12	+12		-6+10	-10+6
final					

Phase II:

initial					
change					
final					

Dynamic Equilibrium

"The Pennies"

Phase I ends with a closing balance illustrated in red and a net change of -12 for 1X, +12 for 1Y; +4 for 2X and -4 for 2Y

Phase I:

Group	1X	1Y		2X	2Y
Rate	-30%	-10%		-30%	-50%
initial	40	0		20	20
change	-12	+12		-6+10	-10+6
final	28	12		24	16

Phase II:

initial					
change					
final					

Dynamic Equilibrium

"The Pennies"

Phase II starts with the balance from Phase I

	Group	1 X	1 Y		2 X	2 Y
Phase I:	Rate	-30%	-10%		-30%	-50%
	initial	40	0		20	20
	change	-12	+12		-6+10	-10+6
	final	28	12		24	16
Phase II:		-30%	-10%		-25%	-50%
	initial	28	12		24	16
	change					
	final					

Calculate the change and final amounts for your Phase I, which is the initial amount for Phase II. Once you are ready, you can begin and go through Phases 1-4 at your own pace. Stop after Phase 4 and await further instructions..

Pennies Results

Group	IA	IB	IIA	IIB	IIIA	IIIB	IVA	IVB
Rate	-50%	-10%	-25%	-50%	-10%	-50%	-50%	-25%
initial	40	0	20	20	20	20	0	40
change								
final	20	20	25	15	28	12	10	30
	-50%	-10%	-25%	-50%	-10%	-50%	-50%	-25%
initial								
change								
final	12	28	20	13	31	9	12	28
	-50%	-10%	-25%	-50%	-10%	-50%	-50%	-25%
initial								
change								
final	9	31	27	14	33	7	13	27
	-50%	-10%	-25%	-50%	-10%	-50%	-50%	-25%
initial								
change								
final	7	33	27	14	34	6	13	27
	-25%	-50%	-50%	-10%	-50%	-25%	-10%	-50%
initial								
change								
final	22	18	14	26	19	21	25	15
	-25%	-50%	-50%	-10%	-50%	-25%	-10%	-50%
initial								
change								
final	25	15	10	30	14	26	30	10
	-25%	-50%	-50%	-10%	-50%	-25%	-10%	-50%
initial								
change								
final	27	13	8	32	14	26	32	7
	-25%	-50%	-50%	-10%	-50%	-25%	-10%	-50%
initial								
change								
final	27	13	7	33	14	26	33	7

Dynamic Equilibrium

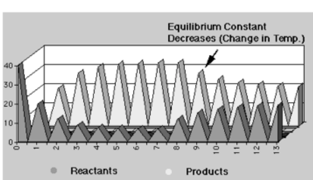
"The Pennies"

Class Results
http://chemconnections.org/general/chem120/equil-graph.html

Simulator:
http://chemconnections.org/Java/equilibrium/

Dynamic Equilibrium

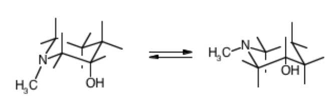
"The Pennies"



http://chemconnections.org/general/chem120/equil-graph.html

Chemical Equilibrium

- *Consider* **A** ⇌ **B**

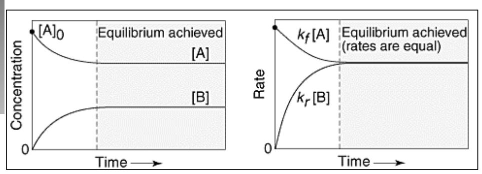


[Refer to the Equilibrium Worksheet.]

- *If the reaction begins with just* **A**, *as the reaction progresses:*
  - **[A]** *decreases to a constant concentration,*
  - **[B]** *increases from zero to a constant concentration.*
  - *When* **[A]** *and* **[B]** *are constant, equilibrium is reached.*

Chemical Equilibrium

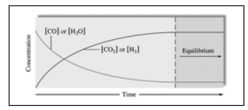
Graphical Treatment of Rates & Changes



- *Rate of loss of A = $-k_f$ [A]; decreases to a constant,*
- *Rate of formation of B = k_r [B]; increases from zero to a constant.*
- *When $-k_f$ [A] = k_r [B] equilibrium is reached.*

QUESTION

The changes in concentrations with time for the reaction $H_2O(g) + CO(g) \leftrightarrows H_2(g) + CO_2(g)$ are graphed below when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed.



Which of the comments given here accurately apply to the concentration versus time graph for the H_2O + CO reaction?

A. The point where the two curves cross shows the concentrations of reactants and products at equilibrium.
B. The slopes of tangent lines to each curve at a specific time prior to reaching equilibrium are equal, but opposite, because the stoichiometry between the products and reactants is all 1:1.
C. Equilibrium is reached when the H_2O and CO curves (green) gets to the same level as the CO_2 and H_2 curves (red) begin.
D. The slopes of tangent lines to both curves at a particular time indicate that the reaction is fast and reaches equilibrium.

Chemical Equilibrium

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

- *Add nitrogen and hydrogen gases together in any proportions. Nothing noticeable occurs.*
- *Add heat, pressure and a catalyst, you smell ammonia => a mixture with constant concentrations of N_2 , H_2 and NH_3 is produced.*
- *Start with just ammonia and catalyst. N_2 and H_2 will be produced until a state of equilibrium is reached.*
- *As before, a mixture with constant concentrations of nitrogen, hydrogen and ammonia is produced.*

Chemical Equilibrium

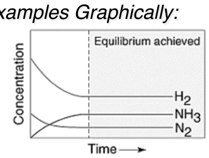
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

No matter what the starting composition of reactants and products, the same ratio of concentrations is realized when equilibrium is reached at a certain temperature and pressure.

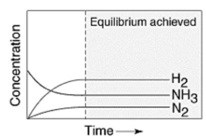
Chemical Equilibrium

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

The Previous Examples Graphically:

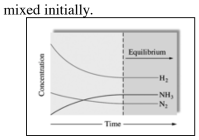


(a)



QUESTION

This is a concentration profile for the reaction $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ when only $N_2(g)$ and $H_2(g)$ are mixed initially.



The figure shown here represents the concentration versus time relationship for the synthesis of ammonia (NH_3). Which of the following correctly interprets an observation of the system?

A. At equilibrium, the concentration of NH_3 remains constant even though some is also forming N_2 and H_2, because some N_2 and H_2 continues to form NH_3.
B The NH_3 curve (red) crosses the N_2 curve (blue) before reaching equilibrium because it is formed at a slower rate than N_2 rate of use.
C. All slopes of tangent lines become equal at equilibrium because the reaction began with no product (NH_3).
D. If the initial N_2 and H_2 concentrations were doubled from what is shown here, the final positions of those curves would be twice as high, but the NH_3 curve would be the same.

Law of Mass Action
(Equilibrium Expression)

- *For a reaction:*
  - *jA + kB ⇆ lC + mD*
- *The law of mass action is represented by the Equilibrium Expression: where K is the Equilibrium Constant. (Units for K will vary.)*

$$K = \frac{[C]^l[D]^m}{[A]^j[B]^k}$$

QUESTION

One of the environmentally important reactions involved in acid rain production has the following equilibrium expression. From the expression, what would be the balanced chemical reaction?
Note: all components are in the gas phase.

$$K = [SO_3]/([SO_2][O_2]^{1/2})$$

A. $SO_3(g) \leftrightarrows SO_2(g) + 2O_2(g)$
B. $SO_3(g) \leftrightarrows SO_2(g) + 1/2O_2(g)$
C. $SO_2(g) + 2O_2(g) \leftrightarrows SO_3(g)$
D. $SO_2(g) + 1/2O_2(g) \leftrightarrows SO_3(g)$

Equilibrium Expression

- *$4\ NH_3(g) + 7\ O_2(g) \leftrightarrow 4\ NO_2(g) + 6\ H_2O(g)$*
- *Write the Equilibrium Expression for the reaction. The expression will have either concentration units of mol/L (M), or units of pressure (atm) for the reactants and products. What would be the overall unit for K using Molarity and atm units respectively.*

$$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

K's units = M^{-1} = L/mol or atm^{-1}

QUESTION

Starting with the initial concentrations of:

$[NH_3] = 2.00\ M$; $[N_2] = 2.00\ M$; $[H_2] = 2.00\ M$,

what would you calculate as the equilibrium ratio once the equilibrium position is reached for the ammonia synthesis reaction?

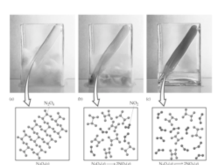
$$N_2 + 3H_2 \leftrightarrows 2NH_3$$

A.1.00
B.0.250
C.4.00
D.This cannot be done from the information provided.

Equilibrium Expressions

- *1) If a reaction is re-written where the reactants become products and products-reactants, the new Equilibrium Expression is the reciprocal of the old.*
  $K_{new} = 1 / K_{original}$
- *2) When the entire equation for a reaction is multiplied by n,*
  $K_{new} = (K_{original})^n$

The Equilibrium Constant



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

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

Initial and Equilibrium Partial Pressures (*P*) of N_2O_4 and NO_2 at 100°C

Experiment	Initial N_2O_4 Partial Pressure (atm)	Initial NO_2 Partial Pressure (atm)	Equilibrium N_2O_4 Partial Pressure (atm)	Equilibrium NO_2 Partial Pressure (atm)	K_{eq}
1	0.0	0.612	0.0429	0.526	6.45
2	0.0	0.919	0.0857	0.744	6.46
3	0.0	1.22	0.138	0.944	6.46
4	0.612	0.0	0.138	0.944	6.46

The Equilibrium Constant

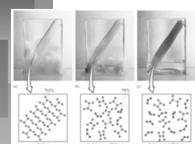
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

$$K_{eq} = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} \quad \text{and} \quad K_{eq} = \frac{(P_{N_2O_4})}{(P_{NO_2})^2}$$

Since their equilibrium expressions are reciprocal to one another, their equilibrium constants are also reciprocals. Point to each expression to see its numerical value at 100°C.

The Equilibrium Constant



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

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$$

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

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72$$

QUESTION

One of the primary components in the aroma of rotten eggs is H_2S. At a certain temperature, it will decompose via the following reaction.

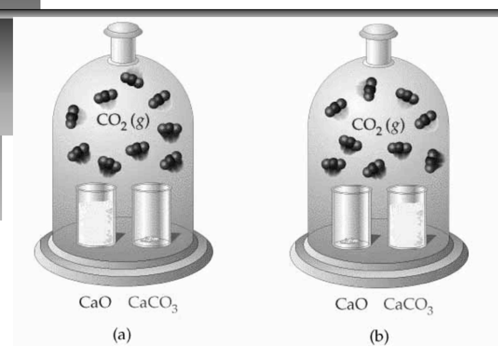
$$2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g)$$

If an equilibrium mixture of the gases contained the following pressures of the components, what would be the value of K_p?

$P_{H_2S} = 1.19$ atm; $P_{H_2} = 0.25$ atm; $P_{S_2} = 0.25$ atm

A.0.011
B.91
C.0.052
D.0.013

Heterogeneous Equilibrium



Heterogeneous Equilibria

- When all reactants and products are in one phase, the equilibrium is homogeneous.
- If one or more reactants or products are in a different phase, the equilibrium is heterogeneous.
  - $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$
  - $K = [CO_2]$

Heterogeneous Equilibria

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

$K = [CO_2]$

- Experimentally, the amount of CO_2 does not meaningfully depend on the amounts of CaO and $CaCO_3$.
- The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.

QUESTION

The liquid metal mercury can be obtained from its ore cinnabar via the following reaction:

$$HgS(s) + O_2(g) \leftrightarrows Hg(l) + SO_2(g)$$

Which of the following shows the proper expression for K_c?

A. $K_c = [Hg][SO_2]/[HgS][O_2]$
B. $K_c = [SO_2]/[O_2]$
C. $K_c = [Hg][SO_2]/[O_2]$
D. $K_c = [O_2]/[SO_2]$

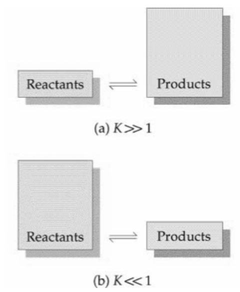
QUESTION

At a certain temperature, FeO can react with CO to form Fe and CO_2. If the K_p value at that temperature was 0.242, what would you calculate as the pressure of CO_2 at equilibrium if a sample of FeO was initially in a container with CO at a pressure of 0.95 atm?

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

A. 0.24 atm
B. 0.48 atm
C. 0.19 atm
D. 0.95 atm

The Equilibrium Constant K



Calculating Equilibrium Constants

- *Tabulate 1) initial and 2) equilibrium concentrations (or partial pressures).*
- *Having both an initial and an equilibrium concentration for any species, calculate its change in concentration.*
- *Apply stoichiometry to the change in concentration to calculate the changes in concentration of all species.*
- *Deduce the equilibrium concentrations of all species.*

$$CH_3COOC_2H_{5(aq)} + H_2O_{(aq)} \rightleftarrows CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

K_c: 5.00 ml of ethyl alcohol, 5.00 ml of acetic acid and 5.00 ml of 3M hydrochloric acid were mixed in a vial and allowed to come to equilibrium. The equilibrium mixture was titrated and found to contain 0.04980 mol of acetic acid at equilibrium. What is the value of K_c ?

1) Calculate the initial molar concentrations (moles are OK in this case).
2) Use the equilibrium concentration of acetic acid to determine the changes and the equilibrium concentrations of the others.
3) Place the equilibrium values into the equilibrium expression to find it's value.

	$CH_3COOC_2H_{5(aq)}$	$+ H_2O_{(aq)}$	$\rightleftarrows CH_3COOH_{(aq)}$	$+ C_2H_5OH_{(aq)}$
Initial (mol)	0	0.261	0.0873	0.0856
Change	+0.0375	+0.0375	-0.0375	-0.0375
Equilibrium	0.0375	0.2985	0.0498	0.0481

0.0873 - 0.0498 = 0.0375

K_c = 0.214

Calculating Equilibrium Constants

- *1) Write the Equilibrium Expression for the hydrolysis of ethyl acetate and calculate **K_c** from the following equilibrium concentrations.*
- *2) Write the Equilibrium Expression for the formation of ethyl acetate from acetic acid and calculate **K_c** from the following equilibrium concentrations.*

Ethyl acetate = 0.01217 M; Ethanol = 0.01623 M
Acetic acid = 0.01750 M ; Water = 0.09267 M

$$CH_3COOC_2H_{5(aq)} + H_2O_{(aq)} \rightleftarrows CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

$$K_c = \frac{[CH_3COOH_{(aq)}]\,[C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]\,[H_2O_{(aq)}]} \qquad K_c = 0.122$$

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \rightleftarrows CH_3COOC_2H_{5(aq)} + H_2O_{(aq)}$$

$$K_c = \frac{[CH_3COOH_{(aq)}]\,[C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]\,[H_2O_{(aq)}]} \qquad K_c = 8.21$$

Calculating K_c from Concentration Data

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

4.00 mol HI was placed in a 5.00 L vessel at 458°C, the equilibrium mixture was found to contain 0.442 mol I_2. What is the value of K_c ? Calculate the molar concentrations, and put them into the equilibrium expression to find it's value.

Initial conc. of HI = $\frac{4.00 \text{ mol}}{5.00 \text{ L}}$ = 0.800 *M*

Equilibrium conc. of I_2 = $\frac{0.442 \text{ mol}}{5.00 \text{ L}}$ = 0.0884 *M*

Conc. (*M*)	**$2HI_{(g)}$** $\rightleftarrows$	**$H_{2\,(g)}$**	**$I_{2\,(g)}$**
Initial	0.800	0	0
Change	- 2x	x	x
Equilibrium	0.800 - 2x	x	x = 0.0884

Calculating K_c from Concentration Data (continued)

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

[HI] = *M* = (0.800 - 2 x 0.0884) *M* = 0.623 *M*

$[H_2]$ = x = 0.0884 *M* = $[I_2]$

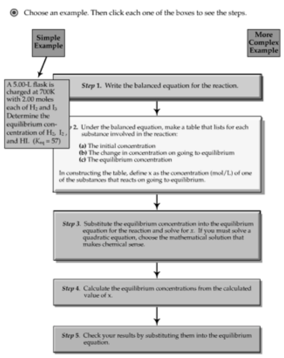
$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2} = \frac{(0.0884)(0.0884)}{(0.623)^2} = 0.0201$$

What does the value 0.0201 mean? Does the decomposition proceed very far under these temperature conditions?

Note: *The initial concentrations, and one at equilibrium were provided. The others that were needed to calculate the equilibrium constant were deduced algebraically.*

Calculation of Equilibrium Concentrations

- *The same steps used to calculate equilibrium constants are used.*
- *Generally, we do not have a number for the change in concentrations line.*
- *Therefore, we need to assume that x mol/L of a species is produced (or used).*
- *The equilibrium concentrations are given as algebraic expressions.Solution of a quadratic equation may be necessary.*



http://chemconnections.org/general/chem120/UsinganEquilibriumTableII.swf

QUESTION

The weak acid $HC_2H_3O_2$, acetic acid, is a key component in vinegar. As an acid the aqueous dissociation equilibrium could be represented as

$$HC_2H_3O_2(aq) \leftrightharpoons H^+(aq) + C_2H_3O_2^-(aq).$$

At room temperature the K_c value, at approximately 1.8×10^{-5}, is not large. What would be the equilibrium concentration of H^+ starting from 1.0 *M* acetic acid solution?

A. 1.8×10^{-5} *M*
B. 4.2×10^{-3} *M*
C. 9.0×10^{-5} *M*
D. More information is needed to complete this calculation.

Equilibrium Concentration Calculations from Initial Concentrations and K_c

The reaction to form HF from hydrogen and fluorine has an equilibrium constant of 115 at temperature T. If 3.000 mol of each component is added to a 1.500 L flask, calculate the equilibrium concentrations of each species.

$$H_{2\,(g)} + F_{2\,(g)} \rightleftharpoons 2\,HF_{(g)}$$

Solution:

$$K_c = \frac{[HF]^2}{[H_2]\,[F_2]} = 115$$

$$[H_2] = \frac{3.000\text{ mol}}{1.500\text{ L}} = 2.000\,M$$

$$[F_2] = \frac{3.000\text{ mol}}{1.500\text{ L}} = 2.000\,M$$

$$[HF] = \frac{3.000\text{ mol}}{1.500\text{ L}} = 2.000\,M$$

Equilibrium Concentration Calculations

$H_{2\,(g)} + F_{2\,(g)} \leftrightharpoons 2\,HF_{(g)}$ *(Continued)*

Concentration (M)	H_2	F_2	HF
Initial	2.000	2.000	2.000
Change	-x	-x	+2x
Final	2.000-x	2.000-x	2.000+2x

$$K_c = \frac{[HF]^2}{[H_2][F_2]} = 115 = \frac{(2.000 + 2x)^2}{(2.000 - x)\,(2.000 - x)} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

Taking the square root of each side:

$$(115)^{1/2} = \frac{(2.000 + 2x)}{(2.000 - x)} = 10.7238$$

x = 1.528

$[H_2]$ = 2.000 - 1.528 = 0.472 *M*
$[F_2]$ = 2.000 - 1.528 = 0.472 *M*
$[HF]$ = 2.000 + 2(1.528) = 5.056 *M*

$$K_c = \frac{[HF]^2}{[H_2][F_2]} = \frac{(5.056\,M)^2}{(0.472\,M)(0.472\,M)}$$

check: $K_c = 115$

Using the Quadratic Equation to solve for an unknown

The gas phase reaction of 2 moles of CO and 1 mole of H_2O in a 1L vessel:

Concentration (*M*)	$CO_{(g)}$	+ $H_2O_{(g)}$ $\rightleftharpoons$	$CO_{2(g)}$	+ $H_{2(g)}$
Initial	2.00	1.00	0	0
Change	-x	-x	+x	+x
Equilibrium	2.00-x	1.00-x	x	x

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(x)\,(x)}{(2.00-x)(1.00-x)} = \frac{x^2}{x^2 - 3.00x + 2.00} = 1.56$$

We rearrange the equation: $0.56\,x^2 - 4.68\,x + 3.12 = 0$

$ax^2 + bx + c = 0$

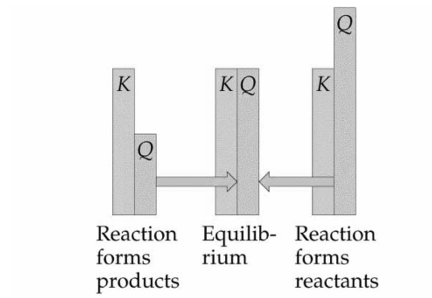
quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{4.68 + \sqrt{(-4.68)^2 - 4(0.56)(3.12)}}{2(0.56)} = 7.6\,M \text{ and } \underline{0.73\,M}$$

[CO] = 1.27 *M*
$[H_2O]$ = 0.27 *M*
$[CO_2]$ = 0.73 *M*
$[H_2]$ = 0.73 *M*

Reaction Quotient (Q) vs. K



K vs. Q: Equilibrium Constants

Has equilibrium been reached?

- *Has equilibrium been reached?* Q *is the "reaction quotient" for any general reaction, for example:*
  - *aA + bB $\rightleftharpoons$ mM + pP*

$$Q = \frac{[M]^{+m}[P]^{+p}}{[A]^{+a}[B]^{+b}}$$

[A], [B], [P], and [M] are Molarities at any time.

Q = K only at equilibrium

Q vs. K: Predicting the Direction of Reaction

- *If Q < K then the forward reaction must occur to reach equilibrium. (i.e., reactants are consumed, products are formed, the numerator in the equilibrium constant expression increases and Q increases until it equals K).*
- *If Q > K then the reverse reaction must occur to reach equilibrium (i.e., products are consumed, reactants are formed, the numerator in the equilibrium constant expression decreases and Q decreases until it equals K).*

Calculating Reaction Direction and Equilibrium Concentrations

Two components of natural gas can react according to the following chemical equation:

$$CH_{4(g)} + 2\,H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_{2(g)}$$

1.00 mol CH_4, 1.00 mol CS_2, 2.00 mol H_2S, and 2.00 mol H_2 are mixed in a 250 mL vessel at 960°C. At this temperature, $K_c = 0.036$.

(a) In which direction will the reaction go?

(b) If [CH_4] = 5.56 M at equilibrium, what are the concentrations of the other substances?

Calculate Q_c and compare it with K_c. Based upon *(a)*, we determine the sign of each component for the reaction table and then use the given [CH_4] at equilibrium to determine the others.

Solution:

$$[CH_4] = \frac{1.00\text{ mol}}{0.250\text{ L}} = 4.00\,M$$

[H_2S] = 8.00 *M*, [CS_2] = 4.00 *M* and [H_2] = 8.00 *M*

Calculating Reaction Direction and Equilibrium Concentrations

$$Q_c = \frac{[CS_2]\,[H_2]^4}{[CH_4]\,[H_2S]^2} = \frac{4.00 \times (8.00)^4}{4.00 \times (8.00)^2} = 64.0$$

Compare Q_c and K_c: $Q_c > K_c$ (64.0 > 0.036, *so the reaction goes to the left. Therefore, reactants increase and products decrease their concentrations*.

(b) Set up the reaction table, with x = [CS_2] that reacts, which equals the [CH_4] that forms.

Concentration (*M*)	$CH_{4\,(g)}$ +	$2\,H_2S_{(g)}$ ⇌	$CS_{2(g)}$ +	$4\,H_{2(g)}$
Initial	4.00	8.00	4.00	8.00
Change	+x	+2x	-x	-4x
Equilibrium	4.00 + x	8.00 + 2x	4.00 - x	8.00 - 4x

Solving for x at equilibrium: [CH_4] = 5.56 *M* = 4.00 *M* + x

x = 1.56 *M*

Calculating Reaction Direction and Equilibrium Concentrations

x = 1.56 *M* = [CH_4]

Therefore:

[H_2S] = 8.00 *M* + 2x = 8.00 *M* + 2(1.56 *M*) = **11.12 *M***

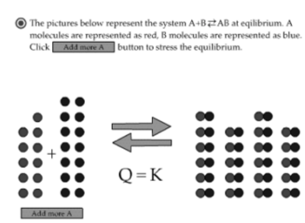
[CS_2] = 4.00 *M* - x = 4.00 *M* - 1.56 *M* = **2.44 *M***

[H_2] = 8.00 *M* - 4x = 8.00 *M* - 4(1.56 *M*) = **1.76 *M***

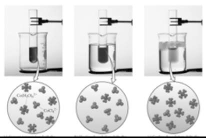
[CH_4] = **1.56 *M***

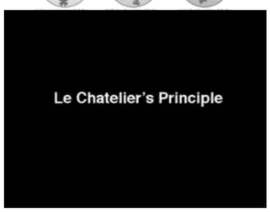
Le Châtelier's Principle

- *. . . if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.*

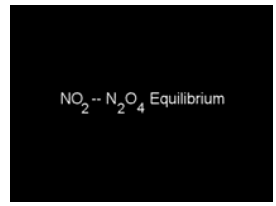


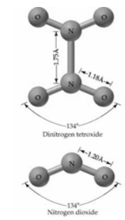
Le Châtelier's Principle



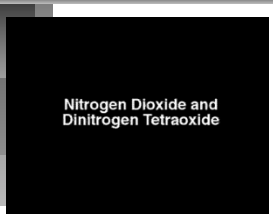


NO_2 - N_2O_4





Temperature Dependence of K



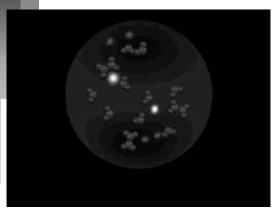
Changes on the System

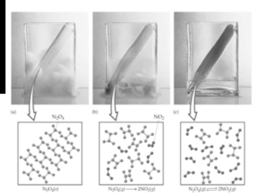
1. Concentration: The system will shift concentrations away from the added component. K remains the same.

2. Temperature: K changes depending upon the reaction.

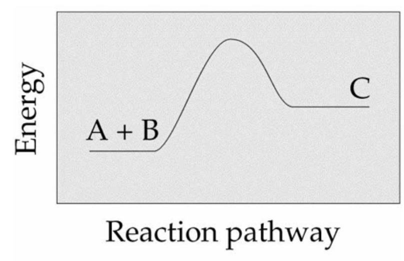
- ***If endothermic, heat is treated as a "reactant", if exothermic, heat is a "product". Endo- > K increases; Exo- > K decreases.***
- ***if ΔH > 0, adding heat favors the forward reaction,***
- ***if ΔH < 0, adding heat favors the reverse reaction.***

Chemical Equilibrium





Which is favored by raising the temperature in the following equilibrium reaction? A+B or C



QUESTION

The following table shows the relation between the value of K and temperature of the system:

At 25°C; $K = 45$; at 50°C; $K = 145$; at 110°C; $K = 467$

(a) Would this data indicate that the reaction was endothermic or exothermic? (b) Would heating the system at equilibrium cause more or less product to form?

A. Exothermic; less product
B. Exothermic; more product
C. Endothermic; less product
D. Endothermic; more product

Changes on the System *(continued)*

- *3. Pressure:*
  - *a. Addition of inert gas does not affect the equilibrium position.*
  - *b. Decreasing the volume shifts the equilibrium toward the side with fewer moles.*
    - $K_p = K_c (RT)^{\Delta n}$

$\Delta n = n_{gas}$ *(products)* - n_{gas} *(reactants)*

- *As the volume is decreased pressure increases.*
- ***Le Châtelier's Principle**: if pressure is increased the system shifts to minimize the increase.*

QUESTION

The balanced equation shown here has a K_p value of 0.011. What would be the value for K_c ?(at approximately 1,100°C)

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

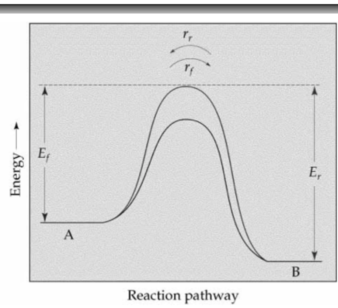
A.0.000098
B.0.011
C.0.99
D.1.2

Changes on the System *(continued)*

4. The Effect of Catalysts

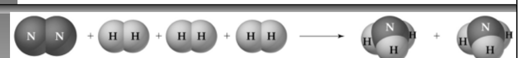
- *A catalyst lowers the activation energy barrier for any reaction….in both forward and reverse directions!*
- *A catalyst will decrease the time it takes to reach equilibrium.*
- *A catalyst* ***does not*** *effect the composition of the equilibrium mixture.*

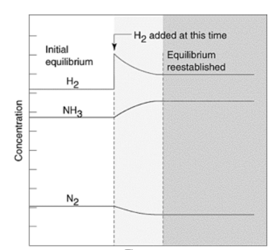
Energy vs. Reaction Pathway



Putting it all Together

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





Putting it all Together

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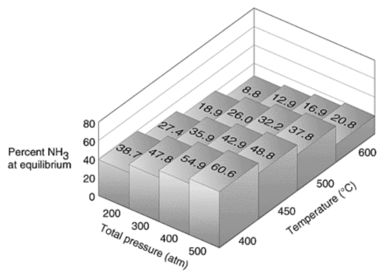

Putting it all Together

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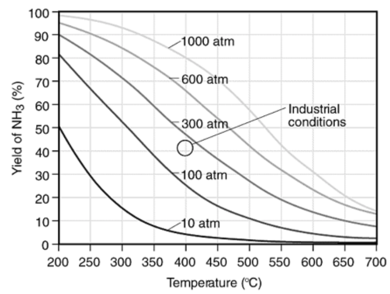

Putting it all Together

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