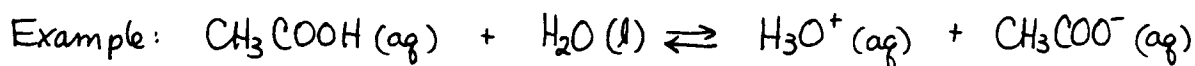


Chapter 17: Chemical Equilibrium

Most reactions do NOT go to completion – unlike the reactions we have looked at so far.

Most reactions attain a state of chemical equilibrium consisting of some mixture of reactants and products. These are called reversible reactions.



or in general terms:



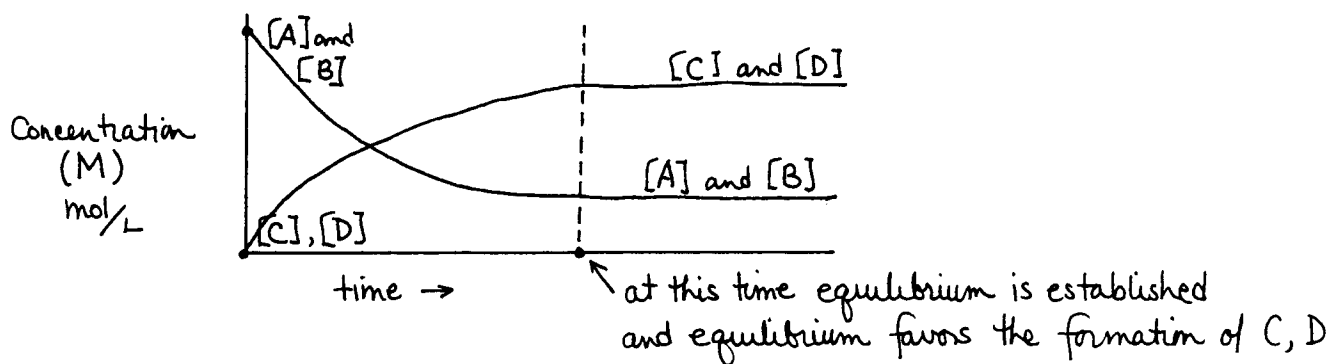
$\rightleftharpoons$ means the reaction is reversible

$\therefore$ both the forward and reverse reactions occur simultaneously

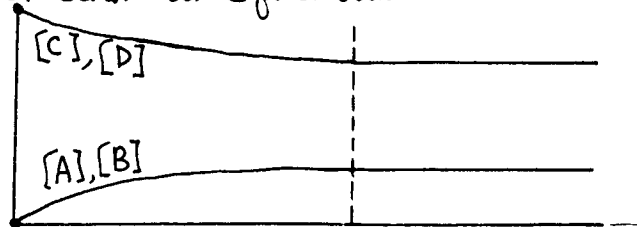
$\therefore$ we have chemical equilibrium: A + B forms C + D at the same rate as C + D forms A + B.

This is a dynamic equilibrium since individual molecules are reacting to form other molecules even though no change in composition can be seen.

If we put equal concentrations of A and B only into a vessel and follow the concentrations of A, B, C, D with time we ^{could} see the following



If we started with equal concentrations of C and D, we end up with the same situation at equilibrium



Let's consider again $A + B \xrightleftharpoons[k_r]{k_f} C + D$ one-step mechanism

for the forward reaction: $\text{Rate} = k_f [A][B]$
 where k_f is forward rate constant

for the reverse reaction: $\text{Rate} = k_r [C][D]$
 where k_r is reverse rate constant

When the rate of the forward reaction is equal to the rate of the reverse reaction, the reaction is at equilibrium.

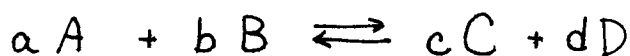
$$\text{Rate forward} = \text{Rate reverse}$$

$$k_f [A][B] = k_r [C][D]$$

$$K_c = \frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

K_c is the EQUILIBRIUM CONSTANT with all products and reactants in concentration units of $\text{mol/liter} = M$.

In more general terms, regardless of what the mechanism is
 Consider

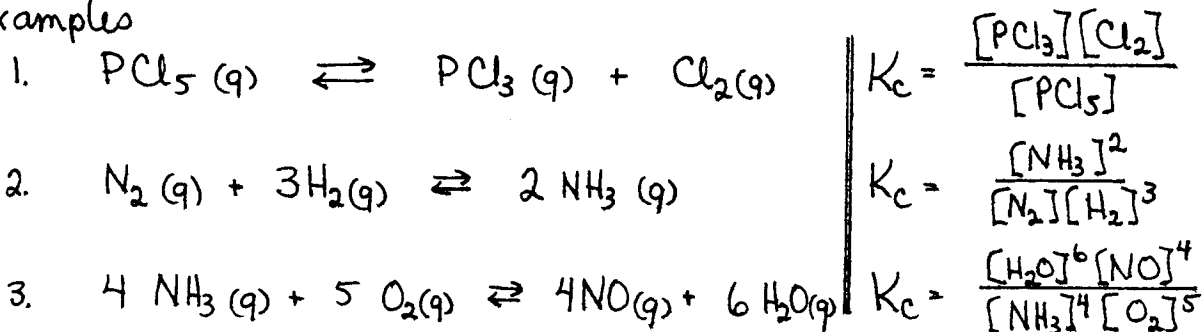


$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

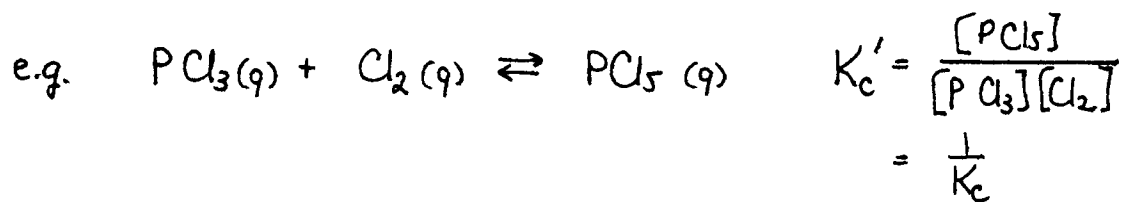
Note: substances in solid (s) or liquid (l) phase are omitted from K_c - only gases (g) and aqueous (aq) substances are included (more later)

K_c is derived from experimental data
 it is a thermodynamic quantity and dependent only on temperature

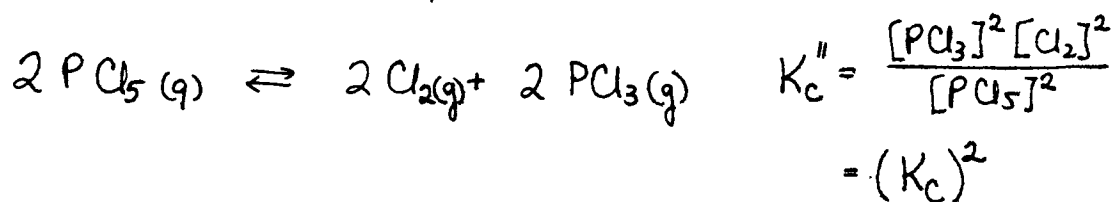
Examples



Note: if a reaction is written backwards, $K_c' = \frac{1}{K_c}$



Question: What is K_c'' for the following?



Example: A 2 liter sample of an equilibrium mixture from a reaction system at a high temperature was found to contain

PCl_3 : 0.344 mol

Cl_2 : 0.172 mol

PCl_5 : 0.056 mol

Calculate K_c using the reaction $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\left(\frac{0.344 \text{ mol}}{2 \text{ L}}\right) \left(\frac{0.172 \text{ mol}}{2 \text{ L}}\right)}{\left(\frac{0.056 \text{ mol}}{2 \text{ L}}\right)}$$

$$= 0.528$$

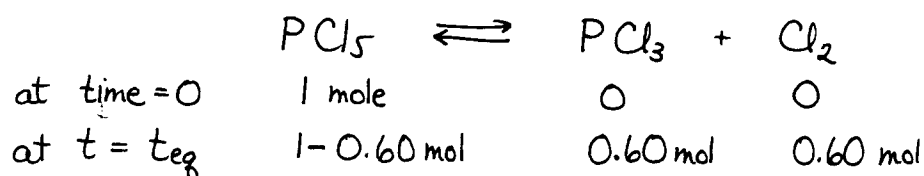
For the reverse reaction, $K_c' = \frac{1}{K_c} = 1.89$

The magnitude of K_c is a measure of the extent of the reaction.

if $K_c \gg 1$: at equilibrium, most of the reactants have been converted to products

if $K_c \ll 1$: at equilibrium, most of the reactants are unreacted and there are very little products

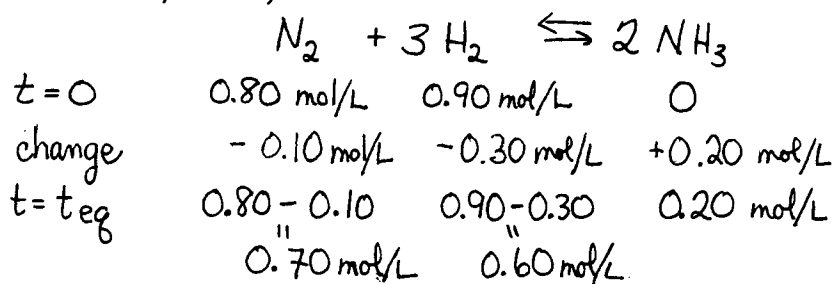
Example: The decomposition of PCl_5 to Cl_2 and PCl_3 was studied at a different temperature. One mole of PCl_5 was put in a 1 liter container and the system was allowed to reach equilibrium. At equilibrium 0.60 moles of PCl_3 was present in the container. What is the equilibrium constant at this temperature (Recall K_c is function of temperature).



At equilibrium, we found 0.60 mol of PCl_3 . To get this, we lost 0.60 mol of PCl_5 . We also gained 0.60 moles of Cl_2 . These calculations are based on the stoichiometry of the reaction.

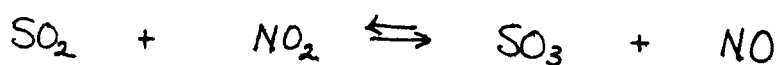
$$\begin{aligned}
 \therefore \text{new } K_c &= \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} \\
 &= \frac{\left(\frac{0.60 \text{ mol}}{1 \text{ L}}\right)\left(\frac{0.60 \text{ mol}}{1 \text{ L}}\right)}{\left(\frac{0.40 \text{ mol}}{1 \text{ L}}\right)} \\
 &= 0.90 \text{ (no units)}
 \end{aligned}$$

Example: At a given temperature, 0.80 mol N_2 and 0.90 mol H_2 were sealed in a 1 l container. At equilibrium 0.20 mol NH_3 was present. Calculate the equilibrium constant, K_c , for this reaction at this temperature (work in $\text{mol/L} \equiv \text{M}$)



$$\begin{aligned}
 \therefore K_c &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \\
 &= \frac{\left[\frac{0.2 \text{ mol}}{1 \text{ L}}\right]^2}{\left[\frac{0.7 \text{ mol}}{1 \text{ L}}\right]\left[\frac{0.6 \text{ mol}}{1 \text{ L}}\right]^3} \\
 &= 0.265
 \end{aligned}$$

Example: The equilibrium constant for the following reaction is 3.00 at a given temperature. If 1.00 mol of SO_2 and 1.00 mol of NO_2 are put into a 2.00 L container and allowed to reach equilibrium, what is the concentration of each compound at equilibrium.



at $t=0$	1.00 mol	1.00 mol	0	0
at $t=t_{\text{eq}}$	$1.00-x$	$1.00-x$	x	x

because all reactants and products have stoichiometric coefficient = 1.

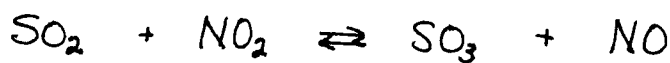
where x = number of moles of $\text{SO}_3 + \text{NO}$ formed

To solve :
$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$= \frac{\left(\frac{x}{2\text{L}}\right)\left(\frac{x}{2\text{L}}\right)}{\left(\frac{1-x}{2\text{L}}\right)\left(\frac{1-x}{2\text{L}}\right)}$$

solve for x and divide by 2 to get concentration.

We can work immediately in concentration units:



$t=0$	$\frac{1.00}{2\text{L}} = 0.5 \text{ M} = \frac{1.00 \text{ mol}}{2\text{L}}$		0	0
-------	---	--	---	---

$t=t_{\text{eq}}$	$0.5-y$	$0.5-y$	y	y
-------------------	---------	---------	-----	-----

where y = concentration of $\text{SO}_3 + \text{NO}$ formed.

$$K_c = \frac{[NO][SO_3]}{[SO_2][NO_2]}$$

$$3.0 = \frac{(y)(y)}{(0.5-y)(0.5-y)}$$

$$\sqrt{3.0} = \sqrt{\frac{y^2}{(0.5-y)^2}}$$

$$1.73 = \frac{y}{0.5-y}$$

$$(0.5-y)1.73 = y$$

$$0.866 - 1.73y = y$$

$$0.866 = 2.73y$$

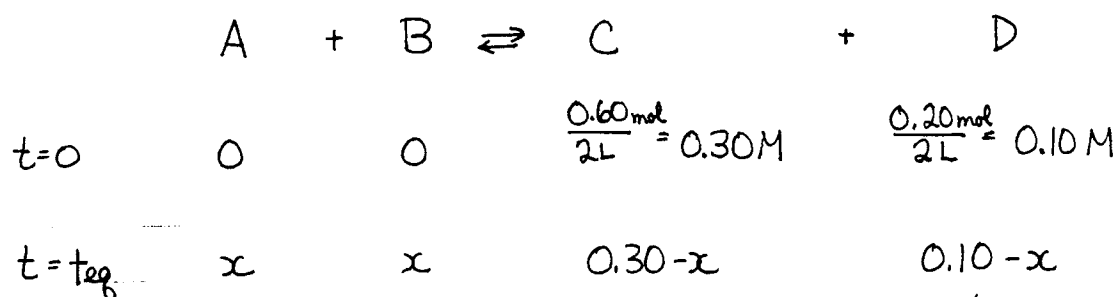
$$y = 0.317 \text{ M} = \text{concentrations of NO, SO}_3$$

$$0.5 - y = 0.183 \text{ M} = \text{concentrations of SO}_2, \text{NO}_2$$

$$\text{The \% dissociation of SO}_2 = \frac{\text{what you lost}}{\text{initial}} \times 100 = \frac{y}{0.5} \times 100 = \frac{0.317}{0.5} \times 100 = 63.4\%$$

Example: The equilibrium constant for the following reaction is 24.0.

Initially, we have 0.60 moles of C and 0.20 moles of D in a 2.00 L container. What are the final concentrations of A, B, C and D?



since the stoichiometric coefficients of each product and reactant = 1.

$$K_c = \frac{[C][D]}{[A][B]}$$

$$24.0 = \frac{(0.30-x)(0.10-x)}{x^2}$$

$$24.0 = \frac{0.030 - 0.40x + x^2}{x^2}$$

$$24x^2 = 0.030 - 0.40x + x^2$$

Rearranging,

$$0 = 23x^2 + 0.40x - 0.030$$

Now, we can solve for x using the quadratic formula!!!

quadratic equation: $ax^2 + bx + c = 0$

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

$\therefore$ in the example

$$x = \frac{-0.40 \pm \sqrt{(0.40)^2 - 4(23)(-0.03)}}{2(23)}$$

$$= \frac{-0.40 \pm 1.71}{46}$$

$$= \frac{-0.40}{46} \text{ and } \underline{\underline{0.028}}$$

IMPOSSIBLE

there is no such
thing as a
negative concentration

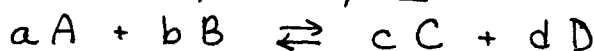
$$\therefore [A] = [B] = x = 0.028 \text{ M}$$

$$[C] = 0.3 - x = 0.272 \text{ M}$$

$$[D] = 0.1 - x = 0.072 \text{ M}$$

Reaction Quotient, Q

Consider this reaction that may or may not be at equilibrium



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{where } [A], [B], [C], [D] \text{ are not necessarily the equilibrium concentrations.}$$

if $Q = K$

the system is at equilibrium

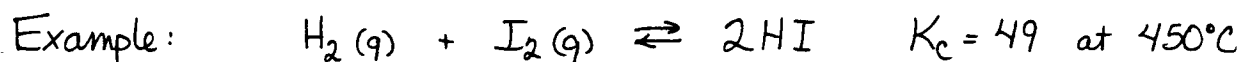
$Q > K$

the amount of products ^(are greater than) exceed what they should be at equilibrium $\therefore$ products will turn into reactants as system approaches equilibrium.

$Q < K$

the amount of reactants exceed ^(are greater than) what they should be at equilibrium $\therefore$ reactants will turn into products as the system approaches equilibrium.

In the real world, situations are very rarely at equilibrium. Knowing Q and what K should be (we can get K by knowing ΔG° for the reaction) will tell us if a system is far from equilibrium.

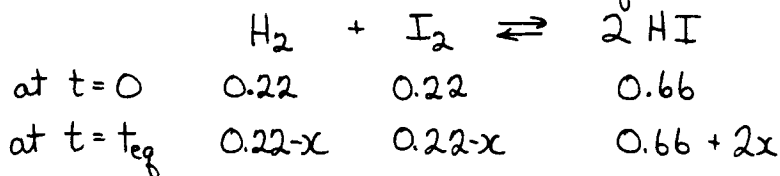


In a container we measure $0.22 \text{ M} = [\text{H}_2] = [\text{I}_2]$ and $[\text{HI}] = 0.66 \text{ M}$
Is the system at equilibrium?

$$Q = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.66)^2}{(0.22)(0.22)} = 9$$

$Q < K_c \quad \therefore$ to approach equilibrium,
we will lose H_2I_2 and gain HI
the forward reaction will occur.

To find the final concentrations at equilibrium -



$$K_c = 49 = \frac{(0.66+2x)^2}{(0.22-x)^2}$$

taking $\sqrt{\quad}$ of both sides

$$7 = \frac{0.66+2x}{0.22-x}$$

$$1.54 - 7x = 0.66 + 2x$$

$$9x = 0.88$$

$$x = 0.098 \text{ M}$$

$$\therefore [\text{H}_2] = [\text{I}_2] = 0.22 - 0.098 = 0.12 \text{ M}$$

$$[\text{HI}] = 0.66 + 2(0.098) = 0.86 \text{ M}$$

Le Chatelier's Principle

If a stress is applied to a system in equilibrium, the equilibrium is shifted in the direction that relieves the stress.

Factors (stresses) that affect Equilibria

① changes in concentration :

we know that as long as the temperature is constant, K_c will be constant.

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

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

if H_2 is added by increasing concentration (or its partial pressure)
more HI will be formed and some I_2 is lost.

if HI is added, more H_2 and I_2 will be formed

if HI is removed, the system will make more HI by converting
 H_2 and I_2 to HI

whatever happens, the system will adjust itself so as to keep
 K_c a constant value (as long as T is constant).
(for example, next page)

② changes in volume by changing total pressure.

Boyle's Law says $P_1V_1 = P_2V_2$ at constant T $\therefore$ as P increases
 V decreases.

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

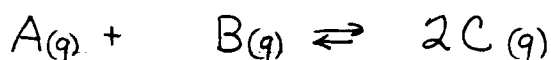
$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

If we increase the total pressure by decreasing volume, the side with
the least # moles of gas is favored and $\therefore$ more N_2O_4 is formed

If we decrease the total pressure by increasing volume, the side
with the most # moles of gas is favored and
 $\therefore$ more NO_2 is formed

Example: Effect of concentration change on equilibrium:

The following system was allowed to reach equilibrium in a 1.00 liter closed container. At this time, the amounts of each substance were found: A, 0.40 moles; B, 0.40 moles; C, 0.80 moles. What are the equilibrium concentrations of A, B and C when 0.60 moles of C are added to the system.



$$t = t_{eq} \quad 0.40 M \quad 0.40 M \quad 0.80 M$$

- we have enough information to calculate K_c :

$$K_c = \frac{[C]^2}{[A][B]} = \frac{(0.80)^2}{(0.40)^2} = 4$$

- when 0.60 mol of C are added to the system, we know from LeChatelier's principle that equilibrium will shift to produce reactants + we will lose some of the C we added.



$t = t_0$	0.40 M	0.40 M	(0.80 + 0.60) = 1.4 M	out of equilibrium
$t = t_{eq}$	+x	+x	-2x	
final equ. conc. ⁿ	0.40 + x	0.40 + x	1.4 - 2x	

Solving for x: $K_c = \sqrt{4} = \sqrt{\frac{(1.4 - 2x)^2}{(0.40 + x)^2}}$

$$2 = \frac{1.4 - 2x}{0.40 + x}$$

$$0.80 + 2x = 1.4 - 2x$$

$$4x = 0.60$$

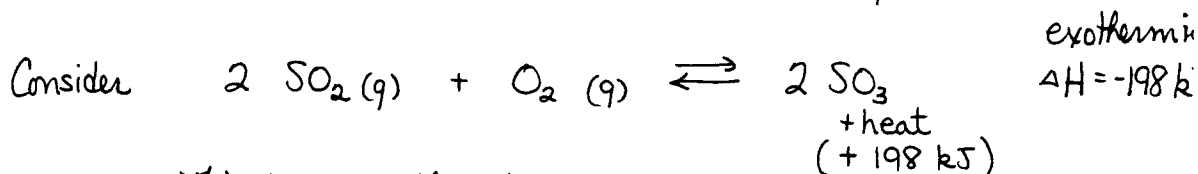
$$x = 0.15$$

$$\therefore [A] = [B] = 0.40 + x = 0.55 M$$

$$[C] = 1.4 - 2x = 1.10 M$$

③ Changes in temperature (K is changing)

The effect is determined by the $\Delta H_{\text{reaction}}$; whether a reaction is exothermic or endothermic affects which direction the equilibrium will shift when heat is added or removed from the system. (treat heat like another product or reactant)



This is an exothermic reaction

$\therefore$ if the temperature is increased, heat is added to the system and more reactants are formed.

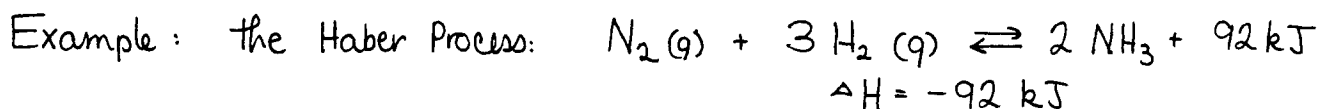
if the temperature is decreased, heat is removed from system and more products are formed.

The opposite is true for an endothermic reaction.

④ Introduction of a catalyst

A catalyst decreases the activation energy, E_a , of both the forward and the reverse reaction equally.

$\therefore$ it does NOT affect equilibrium - only the rate at which equilibrium is reached.



equilibrium will be shifted

- | | | |
|-----|-------------------------------------|---------------|
| (a) | increase T | $\leftarrow$ |
| (b) | increase P (by decreasing V) | $\rightarrow$ |
| (c) | introducing Pt catalyst | no change |
| (d) | force more H_2 into system | $\rightarrow$ |
| (e) | remove NH_3 from system | $\rightarrow$ |
| (f) | lower T | $\rightarrow$ |

* In depth discussion of why volume and temperature changes affect equilibria:

Factor 2: Changes in volume do not affect the value of K_c , but they do change the concentration of the gases

Case 1: $\Delta n_{\text{gas}} \neq 0$ eg. $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ $\Delta n_{\text{gas}} = 1 - 2 = -1$

$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

let us calculate Q for the system when volume is halved

Note: if the volume is halved, concentration is doubled!!

$$Q = \frac{[2 \times \text{N}_2\text{O}_4]}{[2 \times \text{NO}_2]^2} = \frac{2[\text{N}_2\text{O}_4]}{4[\text{NO}_2]^2} = \frac{1}{2} K_c$$

$\therefore Q < K$ and equilibrium will shift to form more products

This result affirms conclusion made earlier: when volume is decreased equilibrium will shift to favor side with fewer moles of gas.

Case 2: $\Delta n_{\text{gas}} = 0$ eg. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ $\Delta n_{\text{gas}} = 0$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

If we calculate Q when volume is halved (concentration is doubled)

$$Q = \frac{[2 \times \text{HI}]^2}{[2 \times \text{H}_2][2 \times \text{I}_2]} = \frac{4[\text{HI}]^2}{4[\text{H}_2][\text{I}_2]} = K \quad \therefore \text{system is still at equilibrium}$$

Factor 3: Changes in temperature DO affect the value of K_c .

What we learned was a quickie way of telling how changes in temperature affect K_c using the value of ΔH .

Example: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ $\Delta H = +3.9 \text{ kJ}$

we remember that $\text{NH}_3(\text{aq})$ is a weak base, $\therefore$ in solution, NH_3 reacts with H_2O only slightly to form $\text{NH}_4^+(\text{aq})$ and $\text{OH}^-(\text{aq})$

$$\therefore K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \text{ is a small number + in fact } = 1.8 \times 10^{-5} \text{ at } 25^\circ\text{C}$$

How does K_c change with temperature? This relationship is given by the van't Hoff Equation:

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Let us find K at 90°C .

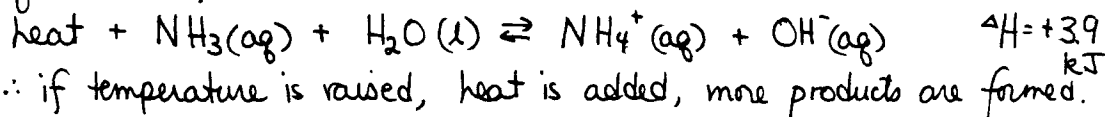
$$\begin{aligned} \log \left(\frac{K_2}{1.8 \times 10^{-5}} \right) &= \frac{+3.9 \times 10^3 \text{ J}}{2.303 \times 8.314 \text{ J/mol K}} \left(\frac{363 - 298}{363 \times 298} \right) \\ &= 0.1224 \\ \frac{K_2}{1.8 \times 10^{-5}} &= 1.326 \end{aligned}$$

$$\begin{aligned} T_2 &= 90 + 273 \\ &= 363 \\ T_1 &= 25 + 273 \\ &= 298 \text{ K} \end{aligned}$$

$$K_2 = 2.4 \times 10^{-5} \quad \therefore K_2 > K_1$$

$\therefore K_2 > K_1$ and there are more products formed at the higher temperature

Our quicker way:

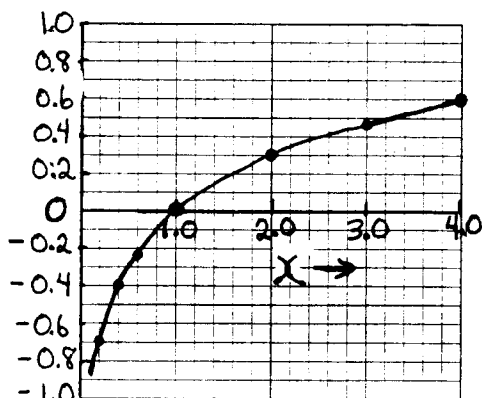


For
your info
Not to be
tested!!

In general, the effect of temperature depends on sign of ΔH° + sign of $(T_2 - T_1)$
 If ΔH , $(T_2 - T_1)$ have same sign, $\log \left(\frac{K_2}{K_1} \right)$ is positive, $\frac{K_2}{K_1} > 1$, $K_2 > K_1$
 If ΔH , $(T_2 - T_1)$ have opposite signs, $\log \left(\frac{K_2}{K_1} \right)$ is negative, $\frac{K_2}{K_1} < 1$, $K_1 > K_2$

RECALL

$\uparrow$
 $\log x$



ΔH + (endothermic) as $T \uparrow$, more products are formed
 as $T \downarrow$, more reactants are formed.

ΔH - (exothermic) as $T \uparrow$, more reactant are formed
 due to Van't Hoff Equation as $T \downarrow$, more product are formed.

Other Representations of the Equilibrium Constant

I K_p , the pressure equilibrium constant

In the laboratory, it is often more convenient to measure partial pressures than concentrations of gases.

We know:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right) RT \quad \text{where} \quad \frac{n}{V} = \frac{\text{moles}}{L} = M$$

Consider $aA + bB \rightleftharpoons cC + dD$ where $A, B, C, D = \text{gases}$

$$\therefore K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{where } P \text{ is in atm. usually}$$

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

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

Now, we have determined K_c for this reaction as well (look back in notes)
How does K_p relate to K_c

$$\begin{aligned} K_p &= \frac{([NH_3] \times RT)^2}{([N_2] \times RT)([H_2] \times RT)^3} \quad \text{since } P = MRT \\ &= \frac{[NH_3]^2}{[N_2][H_2]^3} \times \frac{(RT)^2}{(RT)^4} \\ &= K_c (RT)^{-2} \end{aligned}$$

$$\text{In general} \quad K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$

where R is for gases $0.0821 \frac{\text{Latm}}{\text{mol K}}$ or $62.4 \frac{\text{L torr}}{\text{mol K}}$
 $\Delta n_{\text{gas}} = \text{moles of gaseous products} - \text{gaseous reactants for balanced equation}$