Chemistry 12

Unit II – Dynamic Chemical Equilibrium

KEY

I) General Characteristics

Many chemical reactions are reversible. They have the ability to react in both the forward and reverse direction. One must be careful, however, to distinguish between simply *reversible* reactions and reactions that are not only just reversible, but ***simultaneously*** reversible (ie. reversible reactions that can achieve equilibrium).

Eg. 1: discharging and recharging a car battery

Discharging: $Pb + PbO_2 + 2H^+ + 2HSO_4^- \Rightarrow 2PbSO_4 + 2H_2O$ + energy

- mainly utilized to start the car; can also power other things without the motor running (wipers, stereo, power windows etc…).

Recharging: $2PbSO_4 + 2H_2O$ + energy $\Rightarrow Pb + PbO_2 + 2H^+ + 2HSO_4^-$

- the car's alternator does this while the engine is running – it converts the engine's mechanical energy to electrical energy able to recharge the battery (you will learn much more about this in the Electrochemistry (Redox) unit of Chem. 12).

** while these reactions are reversible, they do NOT occur simultaneously, meaning equilibrium cannot be attained.

Eg. 2: dinitrogen tetroxide and nitrogen dioxide in a closed system

$N_2O_{4(g)}$ + energy $\Rightarrow 2NO_{2(g)}$

$2NO_{2(g)} \Rightarrow N_2O_{4(g)}$ + energy

** these reactions are not only reversible, but they are able to occur simultaneously, thus, equilibrium will eventually be attained.

Knowing this, we can combine the two equations to get:

$N_2O_{4(g)}$ + energy $\Leftrightarrow 2NO_{2(g)}$

double arrows

Closed system: sealed off from surroundings.

Open system: open to surroundings (gases will escape).

Eventually, if left undisturbed in a closed system, the rate of the forward reaction will become equal to the rate of the reverse reaction.

When the rates of the forward and reverse reactions become equal, the reaction is said to have achieved equilibrium.

The Six Characteristics of an Equilibrium System:

1. CLOSED system.

2. Forward reaction rate equals Reverse reaction rate.

3. [Reactants] and [Products] constant (unchanging).
   * usually unequal (unless $\Delta H = 0$ kJ).

4. Macroscopic properties remain constant.
   ie. to the 'unaided eye' it looks as if no changes are occurring.
   * Microscopically, however, changes are occurring (equal rates)
   ↳ DYNAMIC equilibrium (not STATIC)

5. Constant temperature (temp. changes affect K_{eq}).

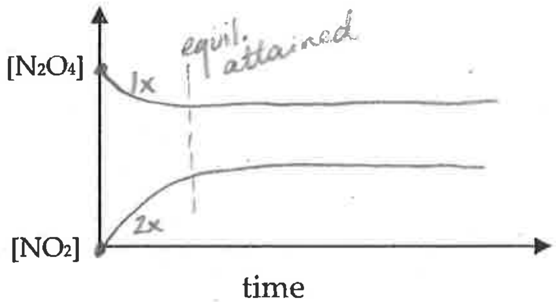
6. Equilibrium can be attained in either direction.

Regardless of the initial concentrations of reactants and products, equilibrium concentrations will always be constant or unchanging.

eg. Graph $[N_2O_4]$ and $[NO_2]$ vs. time for the following reaction:

$$N_2O_{4(g)} + \text{energy} \Leftrightarrow 2NO_{2(g)}$$

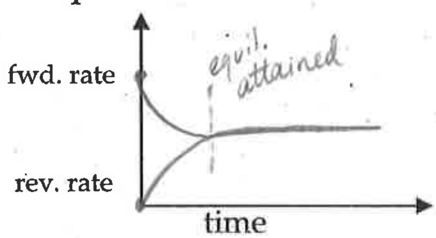
Suppose we start the reaction with only N_2O_4 (the "reactant" in our equation due to the way the reaction is written down).



* Stoichiometry affects the amplitude of [ ] change (see *Note*).
*the final $[N_2O_4]$ and $[NO_2]$ is dependent upon temperature; beyond the scope of Chem. 12 to figure this out

Note: Coefficients refer only to the moles of species actually reacting, not the moles of species merely existing.

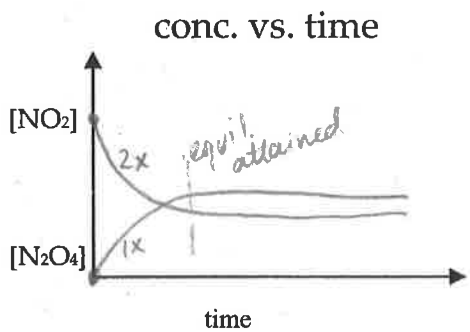
Graph rate vs. time for the previous reaction:

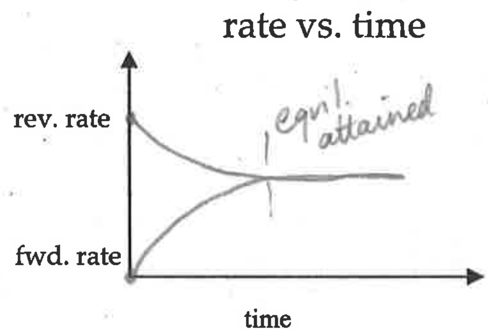


Again, forward and reverse reactions (and rates) are defined by how the rxn is written down.

*For RATE graphs, pay no attention to stoichiometry.

What if we started with NO_2 (the "product") rather than N_2O_4 ?





Questions:

1. Consider the following:
   I. forward and reverse rates are equal ✓
   II. macroscopic properties are constant ✓
   III. can be achieved from either direction ✓
   IV. concentrations of reactants and products are equal ✗ → constant ✓

Which of the above are true for all equilibrium systems?

   A. I and II only
   B. I and IV only
   (C.) I, II, and III only
   D. II, III, and IV only

2. Consider the following equilibrium:

   $N_{2(g)} + 2O_{2(g)} \Leftrightarrow 2NO_{2(g)}$

   Equal moles of N_2 and O_2 are added, under certain conditions, to a closed container. Which of the following describes the changes in the reverse reaction as the system proceeds toward equilibrium?

	Rate of Reverse Reaction	$[NO_2]$
(A.)	increases	increases
B.	decreases	increases
C.	increases	decreases
D.	decreases	decreases

3. Consider the following equilibrium:

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

colourless purple colourless

Which of the following would allow you to conclude that the system has reached equilibrium?

   A. The pressure remains constant * equal moles of gas ; will always be constant
   B. The reaction rates become zero
   (C.) The colour intensity remains constant
   D. The concentrations of all the gases become equal

Quantitative Example of Equilibrium (not testable)

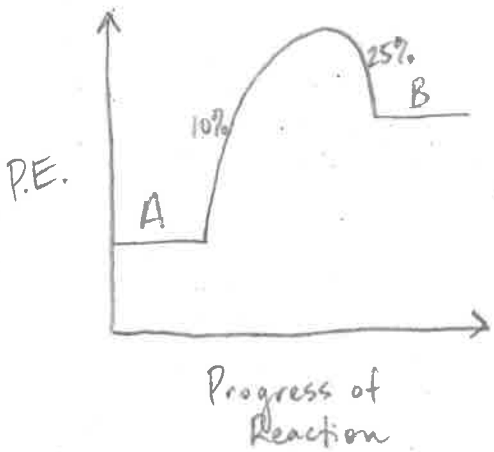
-- students tend to struggle to understand the fact that within an equilibrium reaction, forward and reverse reactions are able to occur at the same rate while [reactant(s)] does not equal [product(s)] (unless ΔH = 0 kJ).

-- the concept of E_a is involved with proving that equilibria exist.

Eg. The following simple equilibrium exists:

$$A \Leftrightarrow B \quad \Delta H = \text{positive}$$

Assume that the reaction begins with 500 molecules of A and 0 of B. Also, 10% of the A molecules attain E_a per minute (collide effectively) while 25% of the B molecules attain E_a per minute. Sketch the PE curve for this reaction. Using your calculator and a table, prove the 'equilibrium theory.'



TIME	# molec. A	# molec. B	# molec. reacting forward	# molec. reacting backward	NET
0	500	0	50	0	50
1	450	50	45	13	32
2	418	82	42	21	21
3	397	103	40	26	14
4	383	117	38	29	9
5	374	126	37	32	5
6	369	131	37	33	4
7	365	135	37	34	3
8	362	138	36	35	1
9	361	139	36	35	1
10	360	140	36	35	1
11	359	141	36	35	1
12	358	142	36	36	0
13	358	142	36	36	0

EQUIL. ACHIEVED!

* 'pooling' on A's side due to higher Ea in fwd. direction.
* more overall collisions required.

Assignment 0: Read pp. 38-39 – Do Qs 3, 5; Read bottom p. 41 – Do Qs 12-13.

II) LeChatelier's Principle

'stress'

If a system at equilibrium is subjected to a change, 'shift' processes will occur to counteract the change until a new equilibrium is achieved.

a) **Concentration Change** $2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)}$

not "amount"

What will happen if more HI is injected into the above equilibrium?

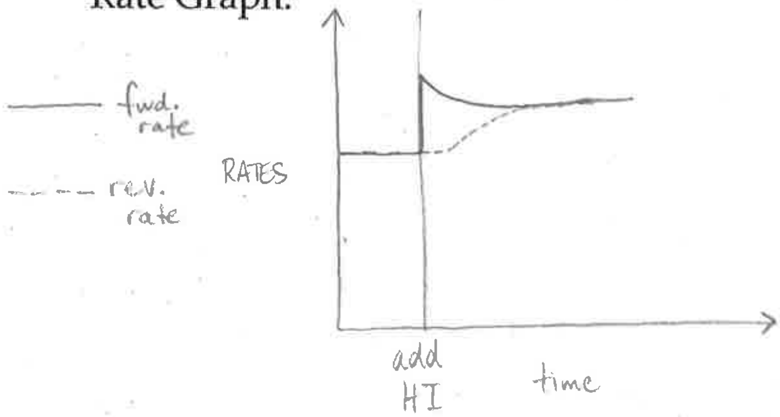
Firstly, since HI is a gas, increasing the moles (amount) of HI also increases the [HI]; this is also the case for aqueous solutions up to their saturation points (next unit), but not for solids and liquids.

So, if more HI is injected into the system, [HI] increases and there will immediately be more HI collisions, thereby ***initially*** increasing the forward rate. The reverse rate ***initially*** remains the same. At this point, we are no longer at equilibrium because the forward rate is temporarily greater than the reverse rate (ie. they are no longer equal, which is the definition of equilibrium). Because H_2 and I_2 are now being produced at a faster rate than they are reacting (ie. forward rate is faster), we say that a **shift** to the RIGHT or to the products occurs (the counteraction of the addition of a substance to the left or reactants' side). Eventually (translation: after the initial changes in rates – meaning *time* passes), more H_2 and I_2 are produced, causing the reverse rate to ***gradually*** increase and because HI reacts faster than it is produced, the forward rate will ***gradually*** decrease (after its initial increase) until the rates are equal again and equilibrium is attained. However, the rates of the forward and reverse reactions at this 'new' equilibrium are higher/increased

*General rule: when [ ] increased on either side, rates go up (more molecules = more collisions); when [ ] decreased on either side, rates go down (less molecules = less collisions).

Shift -- temporary difference in rates (equil. is interrupted), a shift will always occur in the same direction as the faster rate.

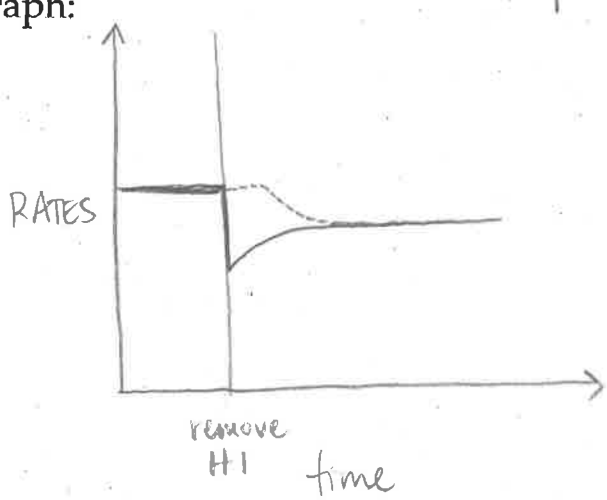
Rate Graph:



In terms of the concentrations of the reaction's species, [HI] initially increases (due to the addition), then gradually decreases (due to the shift), but overall slightly increases. [H_2] gradually increases (due to the shift), and [I_2] gradually increases (due to the shift). *Immediate/initial [ ] changes caused by stresses to rxn ([ ] and pressure changes only); gradual [ ] changes due to shift.

Using the same example above: if HI is removed from the system, [HI] decreases, resulting in less collisions and an initial decrease in the forward rate. The reverse rate initially remains the same. At this point, we are no longer at equilibrium. Because the reverse rate is temporarily faster than the forward rate, a shift to the LEFT occurs. Since HI is being produced faster than it is reacting, the forward rate gradually increases; since H_2 and I_2 are reacting faster than they are being produced, the reverse rate gradually decreases, until both become equal (albeit at a lower rate) – establishing equilibrium.

Rate Graph:



In terms of concentrations: [HI] initally decreases, then gradually increases, but overall slightly decreases. [H_2] and [I_2] both gradually decrease.

Multiple-Choice Time-saver Hint: Increasing the concentration of a substance causes a shift to the opposite side. Decreasing the concentration of a substance causes a shift to the same side.

eg. Consider the following equilibrium:

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

How will the forward and reverse equilibrium reaction rates change when additional H_2 is added to the system?

	Forward Rate	Reverse Rate
A.	Increase	Decrease
B.	Decrease	Increase
(C.)	Increase	Increase
D.	Decrease	Decrease
E.	No Change	No Change

***Warning**!!! Pay attention to nuances in the language of LeChatelier-type questions, such as:
Using the same equilibrium equation above, how will the forward and reverse equilibrium reaction rates change after the addition of H_2 *as the system approaches* equilibrium? Use the same table of answers provided above to get your answer.

Answer this time will be B.

b) Temperature Change

$$2NO_{(g)} + Cl_{2(g)} \Leftrightarrow 2NOCl_{(g)} + 76kJ$$

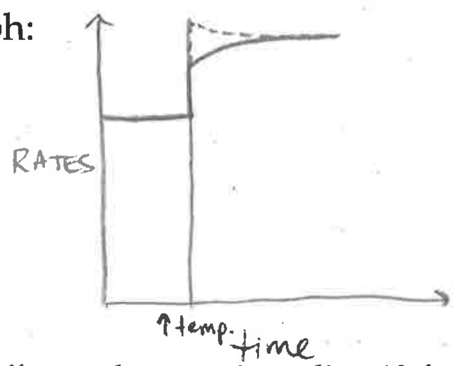
We can subject the above equilibrium to a change by increasing the temperature and subsequently the amount of heat energy in the system. Because the reverse reaction is ENDO thermic, it relies on energy **more** in order to react (higher E_a to overcome). An increase in temperature will increase both rates, but the reverse rate will increase to a greater extent relative to what it once was. Since the rate of the forward reaction is Slower than the reverse rate, there is a shift to the LEFT side (the counteraction, in simple terms) until rates eventually become equal again, establishing a new equilibrium. What has happened to both rates, and why?

Forward Rate: initially increase; gradually increase more ⇒ overall ↑

Overall: both rates ↑ (and equal)

Reverse Rate: initially increase; gradually decrease ⇒ overall ↑

Rate Graph:



*know the difference between ***immediate*** (default in language) and ***gradual*** (must be mentioned in question) temperature changes (re: rate graphs)…

Due to the shift, what will happen to [NO]? ↑

[Cl_2]? ↑

[NOCl]? ↓

} shift (L)

All of these [ ] changes are GRADUAL. There are no IMMEDIATE [ ] changes with temperature changes.

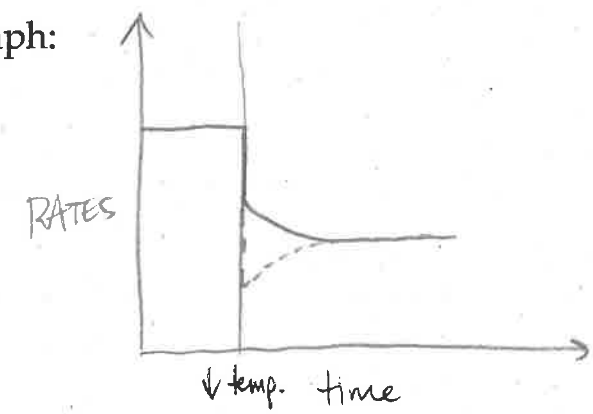
Suppose the temperature is **decreased** - the amount of heat energy in the system decreases. Both forward and reverse rates will decrease, but the reverse rate will decrease to a greater extent relative to what it once was, as it is more dependent on energy. Since the reverse rate is now Slower than the forward rate, there is a shift to the RIGHT side (the counteraction) until a new equilibrium is established. What has happened to both rates, and why?

Forward Rate: initially decrease; gradually decrease more ⇒ overall ↓

Overall: both rates ↓ (and equal)

Reverse Rate: initially decrease; gradually increase ⇒ overall ↓

Rate Graph:



Because of the shift, what will happen to [NO]? ↓

[Cl_2]? ↓

[NOCl]? ↑

} shift (R)

What is the only instance where a temperature change would NOT result in a shift? Where $\Delta H = 0$ kJ

Multiple-Choice Time-saver Hint: Decreasing temperature results in a shift in the exothermic **direction. Increasing temperature results in a shift in the** endothermic **direction.**

c) **Pressure Change**

Pressure changes affect only gaseous substances. Pressure can be altered by altering the volume of the reaction vessel.

A decrease in volume = an increase in pressure and vice versa.

If pressure is increased, then the concentrations of all gases will initially/immediately increase.

Why? Concentration = $\frac{mol}{V}$; if V ↓, then conc. ↑

Similarly, a decrease in pressure will cause an immediate decrease in all gas concentrations. Why?

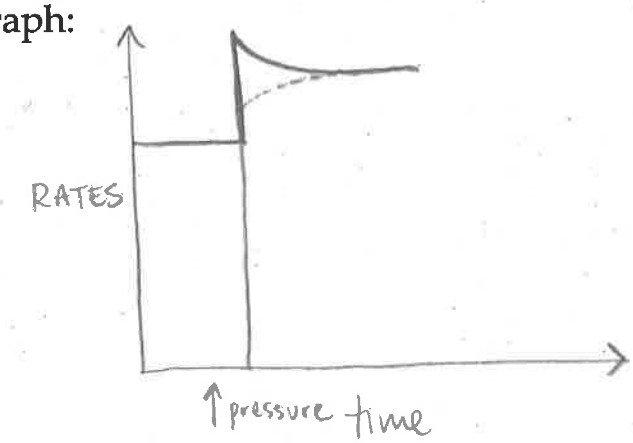
[ ] = $\frac{mol}{V}$; if V ↑, then [ ] ↓.

A change in pressure *might* (**not** *will*) also result in a shift in the equilibrium. An increase in pressure will cause more total collisions for both the forward and reverse reactions, so both rates will increase. However, the side of the reaction involving more gas molecules (or moles) REACTING (see stoichiometry) will increase to a greater extent, causing one rate to be temporarily higher than the other.

Eg. "The Haber Process": $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

An increase in pressure initially (immediately) causes all gas concentrations to Increase, thus increasing both forward and reverse rates. The reactants possess more gas molecules reacting, therefore the forward rate will increase more than the reverse rate, causing a shift to the RIGHT side. As the system approaches equilibrium, the forward rate gradually ↓, while the reverse rate gradually ↑ (more) until they become equal again, albeit at a higher rate.

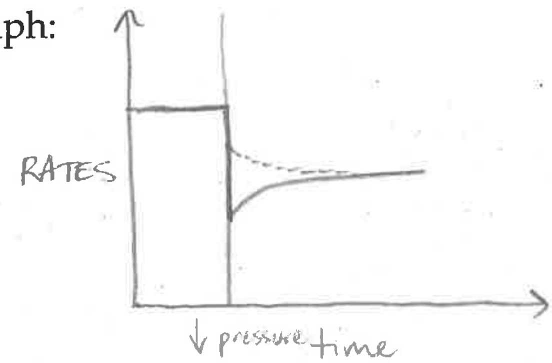
Rate Graph:



In terms of concentrations of reactants and products, [NH_3] will initially increase, then gradually increase more → overall increase. [N_2] and [H_2] will initially increase, then gradually decrease → overall increase.

A decrease in pressure will initially reduce all gas concentrations, and a shift to the side with more gas molecules reacting will take place. More specifically, a decrease in pressure decreases both rates, but decreases the forward rate more as it involves more gas molecules reacting. Thus, the reverse rate is faster causing a shift to the LEFT. As the system approaches equilibrium, the forward rate gradually ↑ and the reverse rate gradually ↓ until they become equal again at a new equilibrium.

Rate Graph:



In terms of concentrations of reactants/products, [NH_3] will initially decrease, then gradually decrease more → overall decrease. [N_2] and [H_2] will initially decrease, then gradually increase → overall decrease.

eg. Why would an increase in pressure not affect the *equilibrium* of the following reaction? $H_{2(g)} + CO_{2(g)} \Leftrightarrow H_2O_{(g)} + CO_{(g)}$
What would happen to both rates? What would happen to the concentration of all species?

i) Equal moles of gas reacting on either side.
ii) both rates would increase, but equally (initially) ∴ NO SHIFT
iii) All [ ]s ↑ due to incr. pressure only.
∴ immediate ↑, no gradual [ ] changes. (no shift)

Addition of an inert (unreactive) gas to an equilibrium system will not affect the [reactants] and [products] AND will not shift the equilibrium (results in no increase/decrease in collisions between reactant/product molecules).

Multiple-Choice Time-saver Hint: An increase in pressure will cause a shift to the side with less gas molecules reacting (to lower overall pressure in chamber – the counteraction). A decrease in pressure will cause a shift to the side with more gas molecules reacting (to increase overall pressure in chamber – the counteraction). Addition of an inert gas will NOT affect the equilibrium.

d) **Addition of a Catalyst**

Catalysts speed up both the forward and reverse rates equally, therefore neither is favoured over the other and there is no shift in the equilibrium.

Other important points to consider:

- Equilibrium shifts will only affect the concentrations of gaseous and aqueous substances. Solids and liquids have maximized concentrations. The **amount** of solid and/or liquid in an equilibrium reaction is affected by a shift, but not the concentration. Recall that the concentration of a liquid/solid is its density; if you increase its mass, you also increase its volume (and vice versa).
- If solid or liquid is added to an equilibrium mixture, no shift will occur; equilibrium will be maintained, since no concentration change was introduced, only an *amount* change. *However*, if solid/liquid is added (Surface Area for collisions is increased), then both forward and reverse rates increase equally and simultaneously (vice versa if solid/liquid is reduced (S.A. is decreased)) – therefore, no shift.

eg. Consider the following equilibrium:

$NH_4Cl_{(s)} \Longleftrightarrow NH_{3\,(g)} + HCl_{(g)}$

Solid Ammonium chloride is added to the above equilibrium reaction. What will happen to both the forward and reverse rates?

	Forward Rate	**Reverse Rate**
A.	No Change	No Change
(B.)	Increase	Increase
C.	Decrease	Decrease
D.	Increase	Decrease
E.	Decrease	Increase

equally and simultaneously

REMEMBER: A shift to the right (favouring products) means that for a time the forward rate is __FASTER__ than the reverse rate, and a shift to the left (favouring reactants) means that for a time the reverse rate is __FASTER__ than the forward rate. If the system is left undisturbed, the rates will eventually become even again, signaling a new equilibrium.

Assignment 1: Le Chatelier Exercises (Arrow Diagrams – not to scale)

1) $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$ $\quad \Delta H = -192kJ$

Stress	**Shift**	**[SO_2]**	**[O_2]**	**[SO_3]**	**Fwd. Rate**	**Rev. Rate**
Increase temperature	L	– ↑ = ↑	– ↑ = ↑	– ↓ = ↓	↑ ↑ = ↑	↑ ↓ = ↑
Decrease pressure	L	↓ ↑ = ↓	↓ ↑ = ↓	↓ ↓ = ↓	↓ ↑ = ↓	↓ ↓ = ↓
Inject more O_2	R	– ↓ = ↓	↑ ↓ = ↑	– ↑ = ↑	↑ ↓ = ↑	– ↑ = ↑
Remove SO_2	L	↓ ↑ = ↓	– ↑ = ↑	– ↓ = ↓	↓ ↑ = ↓	– ↓ = ↓
Add a catalyst	—	—	—	—	↑ – = ↑	↑ – = ↑
Inject $Ar_{(g)}$	—	—	—	—	—	—

2. $Ag_2CrO_{4(s)}$ + heat ⇔ $2Ag^+_{(aq)}$ + $CrO_4^{2-}{}_{(aq)}$

Stress	**Shift**	**[Ag_2CrO_4]**	**[Ag^+]**	**[CrO_4^{2-}]**	**Fwd. Rate**	**Rev. Rate**
Add $Ag_2CrO_{4(s)}$	—	—	—	—	↑–=↑	↑–=↑
Decrease temperature	L	—	–↓=↓	–↓=↓	↓↑=↓	↓↓=↓
Increase pressure	—	—	—	—	—	—
Decrease $Ag^+_{(aq)}$	R	—	↓↑=↓	–↑=↑	–↓=↓	↓↑=↓
Increase $CrO_4^{2-}{}_{(aq)}$	L	—	–↓=↓	↑↓=↑	–↑=↑	↑↓=↑

3. $CH_{4\,(g)}$ + $2H_2S_{(g)}$ + heat ⇔ $CS_{2\,(g)}$ + $4H_{2\,(g)}$

Stress	**Shift**	**[CH_4]**	**[H_2S]**	**[CS_2]**	**[H_2]**	**Fwd. Rate**	**Rev. Rate**
Increase temp.	R	–↓=↓	–↓=↓	–↑=↑	–↑=↑	↑↓=↑	↑↑=↑
Decr. Pressure	R	↓↓=↓	↓↓=↓	↓↑=↓	↓↑=↓	↓↓=↓	↓↑=↓
Add Catalyst	—	—	—	—	—	↑–=↑	↑–=↑
Remove H_2	R	–↓=↓	–↓=↓	–↑=↑	↓↑=↓	–↓=↓	↓↑=↓
Decrease Volume	L	↑↑=↑	↑↑=↑	↑↓=↑	↑↓=↑	↑↑=↑	↑↓=↑

4. $CO_{(g)}$ + $H_2O_{(g)}$ ⇔ $CO_{2(g)}$ + $H_{2(g)}$ $\Delta H = -41kJ$

Stress	**Shift**	**[CO]**	**[H_2O]**	**[CO_2]**	**[H_2]**	**Fwd. Rate**	**Rev. Rate**
Add $CO_{2(g)}$	L	–↑=↑	–↑=↑	↑↓=↑	–↓=↓	–↑=↑	↑↓=↑
Decrease temp.	R	–↓=↓	–↓=↓	–↑=↑	–↑=↑	↓↓=↓	↓↑=↓
Remove $H_2O_{(g)}$	L	–↑=↑	↓↑=↓	–↓=↓	–↓=↓	↓↑=↓	–↓=↓
Increase volume	—	↓–=↓	↓–=↓	↓–=↓	↓–=↓	↓–=↓	↓–=↓
Add $H_{2(g)}$	L	–↑=↑	–↑=↑	–↓=↓	↑↓=↑	–↑=↑	↑↓=↑
Incr. pressure	—	↑–=↑	↑–=↑	↑–=↑	↑–=↑	↑–=↑	↑–=↑
Remove $CO_{2(g)}$	R	–↓=↓	–↓=↓	↓↑=↓	–↑=↑	–↓=↓	↓↑=↓

Assignment 2: Hebden p. 54 #17-23

-QUIZ 1-

Assignment 2 : Better Answers than Text...

17. $N_2O_{3(g)} \rightleftharpoons NO_{(g)} + NO_{2(g)}$

	SHIFT	$[N_2O_3]$	$[NO]$	$[NO_2]$	FWD. RATE	REV. RATE
a) ↑ $[NO]$	L	– ↑ = ↑	↑ ↓ = ↑	– ↓ = ↓	– ↑ = ↑	↑ ↓ = ↑
b) ↑ $[N_2O_3]$	R	↑ ↓ = ↑	– ↑ = ↑	– ↑ = ↑	↑ ↓ = ↑	– ↑ = ↑
c) ↑ pressure	L	↑ ↑ = ↑	↑ ↓ = ↑	↑ ↓ = ↑	↑ ↑ = ↑	↑ ↓ = ↑
d) add catalyst	—	—	—	—	↑ – = ↑	↑ – = ↑

18. $2\,H_{2(g)} + 2\,NO_{(g)} \rightleftharpoons N_{2(g)} + 2\,H_2O_{(g)}$

	SHIFT	$[H_2]$	$[NO]$	$[N_2]$	$[H_2O]$	FWD. RATE	REV. RATE
a) ↓ $[N_2]$	R	– ↓ = ↓	– ↓ = ↓	↓ ↑ = ↓	– ↑ = ↑	– ↓ = ↓	↓ ↑ = ↓
b) ↓ $[NO]$	L	– ↑ = ↑	↓ ↑ = ↓	– ↓ = ↓	– ↓ = ↓	↓ ↑ = ↓	– ↓ = ↓
c) ↓ pressure	L	↓ ↑ = ↓	↓ ↑ = ↓	↓ ↓ = ↓	↓ ↓ = ↓	↓ ↑ = ↓	↓ ↓ = ↓

19. $2\,CO_{(g)} + O_{2(g)} \rightleftharpoons 2\,CO_{2(g)} + 566\text{ kJ}$

	SHIFT	$[CO]$	$[O_2]$	$[CO_2]$	FWD. RATE	REV. RATE
a) ↑ temp.	L	– ↑ = ↑	– ↑ = ↑	– ↓ = ↓	↑ ↑ = ↑	↑ ↓ = ↑
b) ↑ $[O_2]$	R	– ↓ = ↓	↑ ↓ = ↑	– ↑ = ↑	↑ ↓ = ↑	– ↑ = ↑
c) add catalyst	—	—	—	—	↑ – = ↑	↑ – = ↑

20. $I_{2(g)} + Cl_{2(g)} \rightleftharpoons 2\,ICl_{(g)}$ $\Delta H = 35.0\text{ kJ}$

	SHIFT	$[I_2]$	$[Cl_2]$	$[ICl]$	FWD. RATE	REV. RATE
a) ↓ temp.	L	– ↑ = ↑	– ↑ = ↑	– ↓ = ↓	↓ ↑ = ↓	↓ ↓ = ↓
b) ↓ $[Cl_2]$	L	– ↑ = ↑	↓ ↑ = ↓	– ↓ = ↓	↓ ↑ = ↓	– ↓ = ↓
c) ↑ pressure	—	↑ – = ↑	↑ – = ↑	↑ – = ↑	↑ – = ↑	↑ – = ↑

21. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H = -92\ kJ$

	SHIFT	$[N_2]$	$[H_2]$	$[NH_3]$	FWD. RATE	REV. RATE
a) ↑ $[N_2]$	R	↑↓=↑	−↓=↓	−↑=↑	↑↓=↑	−↑=↑
b) ↑ temp.	L	−↑=↑	−↑=↑	−↓=↓	↑↑=↑	↑↓=↑
c) ↑ volume	L	↓↑=↓	↓↑=↓	↓↓=↓	↓↑=↓	↓↓=↓
d) add catalyst	—	—	—	—	↑−=↑	↑−=↑

22. $2HF_{(g)} \rightleftharpoons F_{2(g)} + H_{2(g)}$ $\Delta H = 536\ kJ$

	SHIFT	$[HF]$	$[F_2]$	$[H_2]$	FWD. RATE	REV. RATE
a) ↓ temp.	L	−↑=↑	−↓=↓	−↓=↓	↓↑=↓	↓↓=↓
b) ↓ $[H_2]$	R	−↓=↓	−↑=↑	↓↑=↓	−↓=↓	↓↑=↓
c) ↓ volume	—	↑−=↑	↑−=↑	↑−=↑	↑−=↑	↑−=↑

23. $SnO_{2(s)} + 2CO_{(g)} \rightleftharpoons Sn_{(s)} + 2CO_{2(g)}$ $\Delta H = 13\ kJ$

	SHIFT	$[SnO_2]$	$[CO]$	$[Sn]$	$[CO_2]$	FWD. RATE	REV. RATE
a) ↑ temp.	R	—	−↓=↓	—	−↑=↑	↑↓=↑	↑↑=↑
b) add catalyst	—	—	—	—	—	↑−=↑	↑−=↑
c) ↑ $[CO]$	R	—	↑↓=↑	—	−↑=↑	↑↓=↑	−↑=↑

III) Equilibrium Concentration Graphs

Equilibrium concentration graphs show how a stress affects the concentration of species in an equilibrium in a graphical manner, with respect to [reactants] and [products]. Changes are to relative scale, unlike arrow diagrams. Do not confuse with *rate* graphs!

Rules:

1) Solid and liquid concentrations always remain constant.
2) Changes due to temperature are all gradual.
3) Changes in pressure result in equal (in ratio (see rule 4 below)), rapid changes in all gas concentrations initially, and then possible gradual changes (based on stoichiometry).
4) Immediate changes due to pressure changes do NOT depend on stoichiometry, but rather the initial molarity before the volume change. The ratio of the change is the same (since K_{eq} remains constant during pressure stresses).

eg. double the volume of 3M and 4M solutions:

$\frac{3\ mol}{2\ L} = 1.5\ M$ (down 1.5M); $\frac{4\ mol}{2\ L} = 2.0\ M$ (down 2 M)

but, ratio of change same ⇒ down by half.

5) Changes due to addition or removal of substances (gaseous and/or aqueous) are first immediate for that substance only, and then gradual for all substances, including the originally altered substance.
6) Label your gradual concentration changes on your graphs using the stoichiometry as your guide (eg. 1x, 2x, 3x, etc…).

Example: Graph the result of the stresses applied to the following equilibrium system: $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} + \text{energy}$

a) increase in temperature

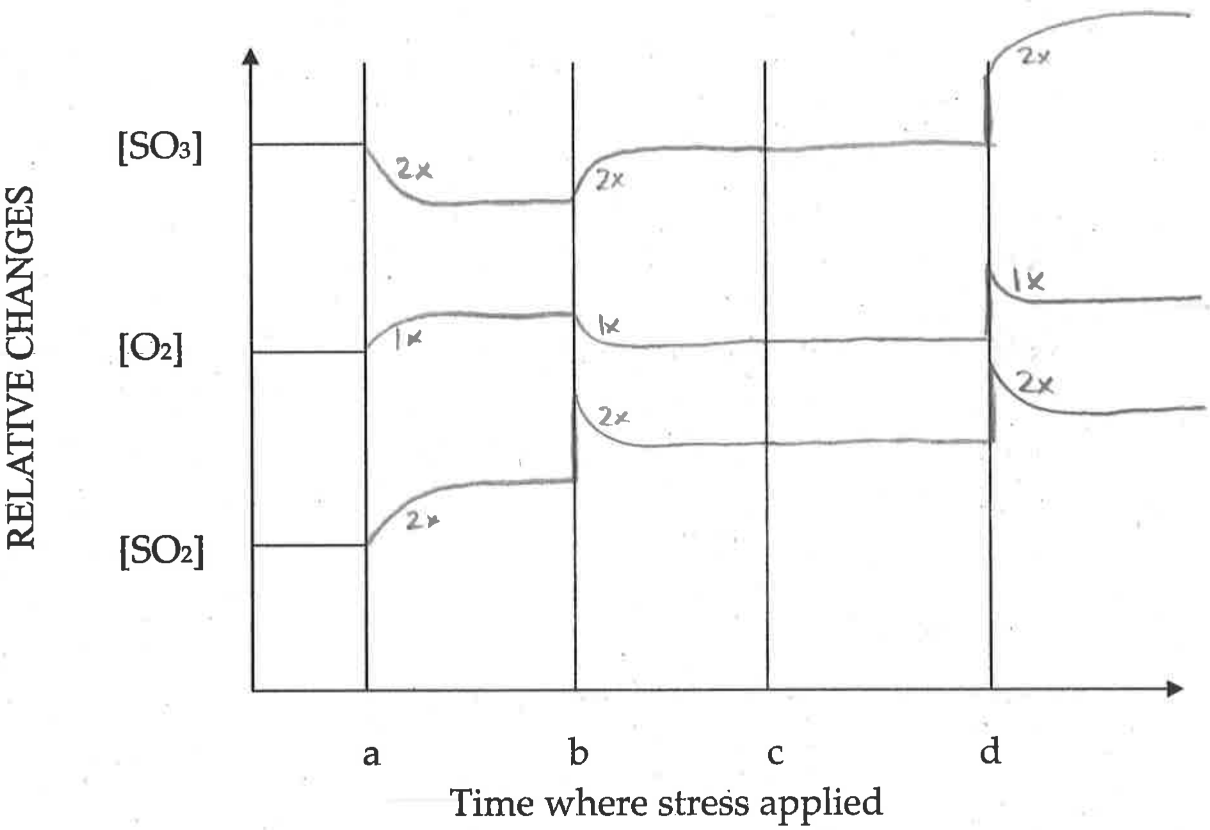
b) add $SO_{2(g)}$

c) add a catalyst

d) decrease volume

Use an arrow diagram to help (optional):

STRESS	SHIFT	$[SO_2]$	$[O_2]$	$[SO_3]$
↑ temp.	L	– ↑ = ↑	– ↑ = ↑	– ↓ = ↓
↑ $[SO_2]$	R	↑↓ = ↑	– ↓ = ↓	– ↑ = ↑
CATALYST	—	—	—	—
↓ Volume	R	↑↓ = ↑	↑↓ = ↑	↑↑ = ↑



i. Stoichiometry does NOT affect IMMEDIATE changes;

ii. Stoichiometry DOES affect GRADUAL changes.

Assignment 3: Draw concentration graphs for each.

1) $2C_{(s)} + O_{2(g)} \Leftrightarrow 2CO_{(g)}$ $\Delta H = -97kJ$

stresses: a) decrease volume c) add CO

b) add O_2 d) increase temperature

2) $SO_{3(g)} + NO_{(g)} \Leftrightarrow NO_{2(g)} + SO_{2(g)}$ + energy

stresses: a) increase temperature c) decrease pressure

b) remove some $NO_{2(g)}$

3) $CaCO_{3\,(s)} + 2HF_{(g)} \Leftrightarrow CaF_{2\,(s)} + H_2O_{(g)} + CO_{2\,(g)}$

stresses: a) remove some $CaCO_{3(s)}$ c) add $HF_{(g)}$

b) increase volume

4) $CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$ $\Delta H = +50kJ$

stresses: a) increase temperature d) decrease volume

b) decrease temperature e) add something which reacts with H_2O

c) decrease pressure

Assignment 4: Hebden p. 55 #24-28

– QUIZ –

IV) Predicting Whether a Reaction Will Go to Completion, to Equilibrium, or Not React At All

Relies upon two fundamental principles:

i) **Enthalpy** (Heat): the energy in the system

An endothermic reaction displays **maximum** or **increasing** enthalpy because energy has been gained.

$$N_2O_4 + \text{energy} \Leftrightarrow 2NO_2$$

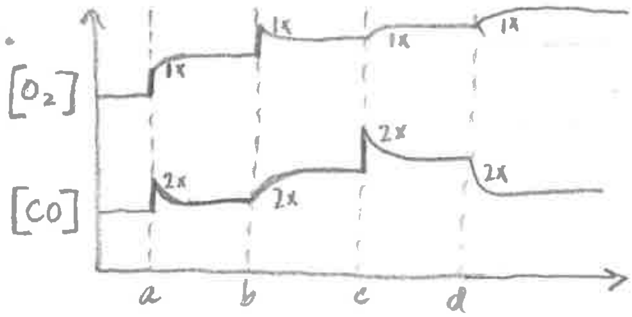
This equilibrium is endothermic in the forward direction.

Therefore, NO_2 has a larger enthalpy (PE – lower stability) than N_2O_4.

Similarly, the above equilibrium is exothermic in the reverse direction because energy is being released. Therefore, enthalpy is **minimum** or **decreasing** in the **exothermic** direction.

Reactions naturally tend toward minimum or decreasing enthalpy, meaning they tend toward the EXOTHERMIC direction. Why? Lower Ea

Assignment 3 - Graphing Exercises

1.


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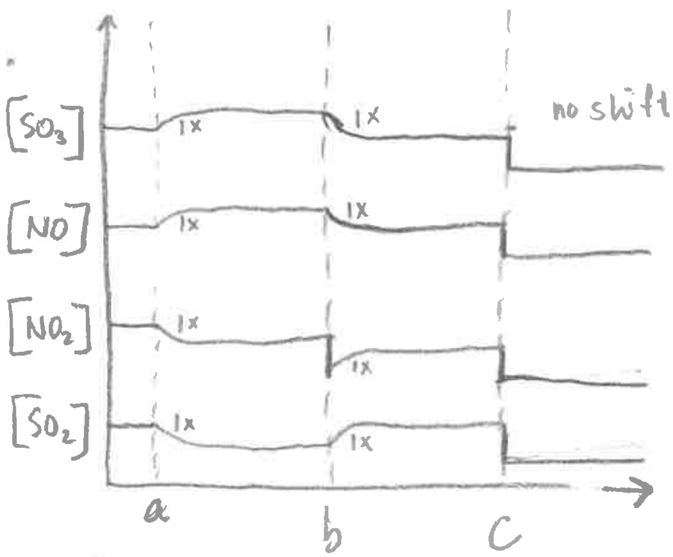

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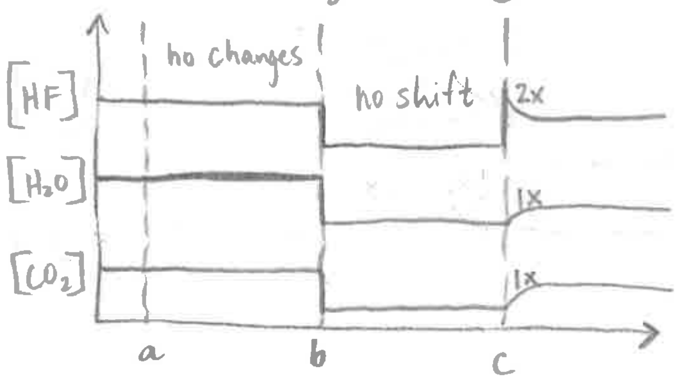
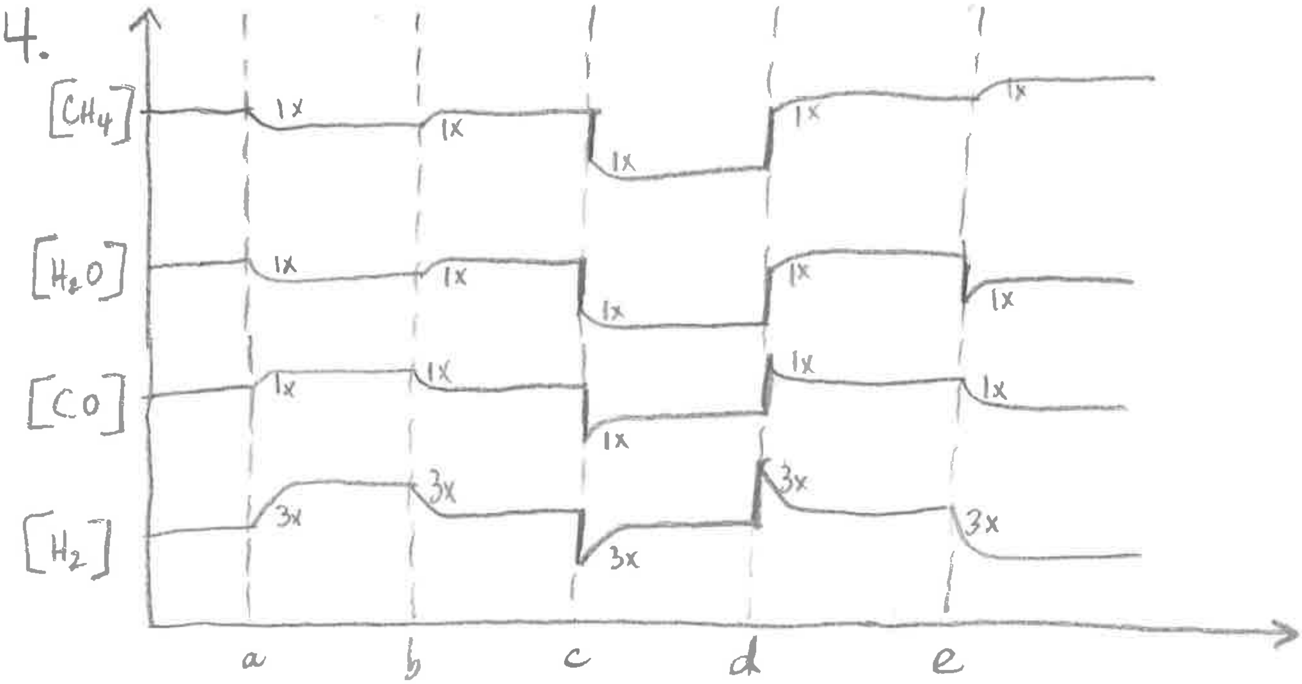


4.



ii) **Entropy**: measure of disorder/chaos

The universe is always increasing its entropy as there are many more disordered arrangements compared to ordered arrangements.

eg. there are more ways for your room to be messy than clean.

MAXIMUM ENTROPY gases >> solutions (aq) >> liquids >> solids MINIMUM ENTROPY

← INCREASING ENTROPY

The side of the reaction possessing the most particles (moles) in the higher entropy phase will be the side displaying maximum entropy.

$$A_{(g)} + B_{(g)} \Leftrightarrow 2C_{(g)} + D_{(g)}$$

Maximum entropy is in the forward direction.

$$A_{(s)} + B_{(g)} \Leftrightarrow 2C_{(l)} + D_{(l)}$$

Maximum entropy is in the reverse direction.

$$A_{(aq)} + B_{(s)} \Leftrightarrow 2C_{(l)} + D_{(l)}$$

Increasing entropy is in the reverse direction.

$$A_{(g)} + B_{(g)} \Leftrightarrow C_{(g)} + D_{(g)}$$

Increasing entropy is in the **unable to predict** direction.

* in the last example, it is beyond the scope of Chem 12 to predict which species (reactants or products) exhibit greater stability.

Reactions naturally tend toward maximum or increasing entropy.

So…to summarize:

Reactions naturally tend toward minimum **or** decreasing **enthalpy and** maximum **or** increasing **entropy.**

Making Predictions

1) A reaction will **spontaneously** go to **completion** if the forward reaction displays minimum or decreasing enthalpy and maximum or increasing entropy.

$$H_2SO_{4(l)} + H_2O_{(l)} \Rightarrow H_2SO_{4(aq)} + 150kJ$$

decr. enthalpy →

incr. entropy →

1st arrow: ↓ enthalpy

2nd arrow: ↑ entropy

Both arrows forward ∴ rxn. to 100% completion.

2) A reaction will **not occur** if the reverse reaction displays minimum enthalpy and maximum entropy.

$$C_2H_{2(g)} + Ca(OH)_{2(aq)} \Rightarrow CaC_{2(s)} + 2H_2O_{(l)} \quad \Delta H = 185kJ$$

$\leftarrow$ $\leftarrow$ } both arrows in reverse ∴ NO REACTION

3) A reaction will come to **equilibrium** if the tendencies toward minimum enthalpy and maximum entropy oppose.

$$C_2H_{6(g)} \Leftrightarrow C_2H_{2(g)} + 2H_{2(g)} \quad \Delta H = 311kJ$$

$\leftarrow$ $\rightarrow$ } opposing arrows ∴ EQUILIBRIUM.

Assignment 5: Reaction Predictions + Try p.48 Qs 14-16.
State whether the following reactions will
(C) – go to completion
(E) – reach equilibrium
(NR) – not react

1st arrow: toward min. enthalpy 2nd arrow: toward max. entropy

1. $4NH_{3(g)} + 5O_{2(g)} \Rightarrow 4NO_{(g)} + 6H_2O_{(g)} \quad \Delta H = +115kJ$ $\leftarrow \rightarrow$ E
2. $N_2O_{4(g)} + 58.9kJ \Rightarrow 2NO_{2(g)}$ $\leftarrow \rightarrow$ E
3. $N_{2(g)} + 3H_{2(g)} \Rightarrow 2NH_{3(g)}$ $\leftarrow \leftarrow$ $\Delta H = +100kJ$ NR
4. $2Bi^{3+}{}_{(aq)} + 3H_2S_{(g)} \Rightarrow BiS_{3(s)} + 6H^+{}_{(aq)}$ + energy $\rightarrow \leftarrow$ E
5. $CaCO_{3(s)} \Rightarrow CaO_{(s)} + CO_{2(g)}$ + energy $\rightarrow \rightarrow$ C
6. $C_{(s)} + H_2O_{(g)} \Rightarrow CO_{(g)} + H_{2(g)}$ + energy $\rightarrow \rightarrow$ C
7. $2Ag_{(s)} + Cl_{2(g)} \Rightarrow 2AgCl_{(s)} \quad \Delta H = -254kJ$ $\rightarrow \leftarrow$ E
8. $2H_2O_{2(aq)} \Rightarrow O_{2(g)} + 2H_2O_{(l)} \quad \Delta H = -189kJ$ $\rightarrow \rightarrow$ C
9. $H_2O_{(g)} + C_{(s)} \Rightarrow CO_{2(g)} + H_{2(g)} \quad \Delta H = +31.3kJ$ $\leftarrow \rightarrow$ E
10. $3C_2H_{2(g)} \Rightarrow C_6H_{6(g)}$ + 143kJ $\rightarrow \leftarrow$ E
11. $NaOH_{(aq)} + 2.4kJ \Rightarrow NaOH_{(s)}$ $\leftarrow \leftarrow$ NR
12. $2Mg_{(s)} + O_{2(g)} \Rightarrow 2MgO_{(s)}$ + 76kJ $\rightarrow \leftarrow$ E
13. $CS_{2(g)} + 3O_{2(g)} \Rightarrow CO_{2(g)} + 2SO_{2(g)}$ + 66kJ $\rightarrow \leftarrow$ E

14. A student predicts that the following reaction will go to completion. Do you agree or disagree? Support your explanation with enthalpy and entropy changes.

$$CO_{(g)} + H_2O_{(l)} \; ?\leftrightarrow? \; CO_{2(g)} + H_{2(g)} \quad \Delta H = 42kJ$$

$\leftarrow \rightarrow$ Disagree; will reach equilibrium. Enthalpy does not support fwd. rxn.

15. For the following reaction, in which direction is enthalpy increasing? In which direction is entropy maximized? Will the reaction reach equilibrium?

$$2C_4H_{10(g)} + 13O_{2(g)} \ ?\leftrightarrow? \ 8CO_{2(g)} + 10H_2O_{(g)} + \text{Energy}$$

i) Reverse

ii) Forward

iii) No ; 100% completion.

16. In order for a chemical reaction to go to completion, how must the entropy and enthalpy change?

	Entropy	Enthalpy
A.	increases	increases
(B.)	increases	decreases
C.	decreases	increases
D.	decreases	decreases

17. In which of the following reactions do the tendencies for minimum enthalpy and maximum entropy both favour reactants?

(A.) $3O_{2(g)} \ ?\leftrightarrow? \ 2O_{3(g)}$ $\Delta H = +285kJ$

B. $N_{2(g)} + 3H_{2(g)} \ ?\leftrightarrow? \ 2NH_{3(g)}$ $\Delta H = -92kJ$

C. $2BrCl_{(g)} \ ?\leftrightarrow? \ Br_{2(g)} + Cl_{2(g)}$ $\Delta H = -29.3kJ$

D. $CaCO_{3(s)} \ ?\leftrightarrow? \ CaO_{(s)} + CO_{2(g)}$ $\Delta H = +175kJ$

V) Haber Process

The Haber Process for making ammonia (NH_3) was developed by German chemist Fritz Haber prior to World War I. Previously, Germany was receiving nitrates from Chile in order to make explosives (TNT). However, these shipping lines were to be cut off once the war began. Haber developed the process to make ammonia using inexpensive N_2 and H_2, which could then be easily converted into nitrates, and subsequently converted into explosives.

$$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)} + 92.4kJ$$

What should the temperature and pressure conditions be in order to maximize the NH_3 produced?

decreased temperature and increased pressure

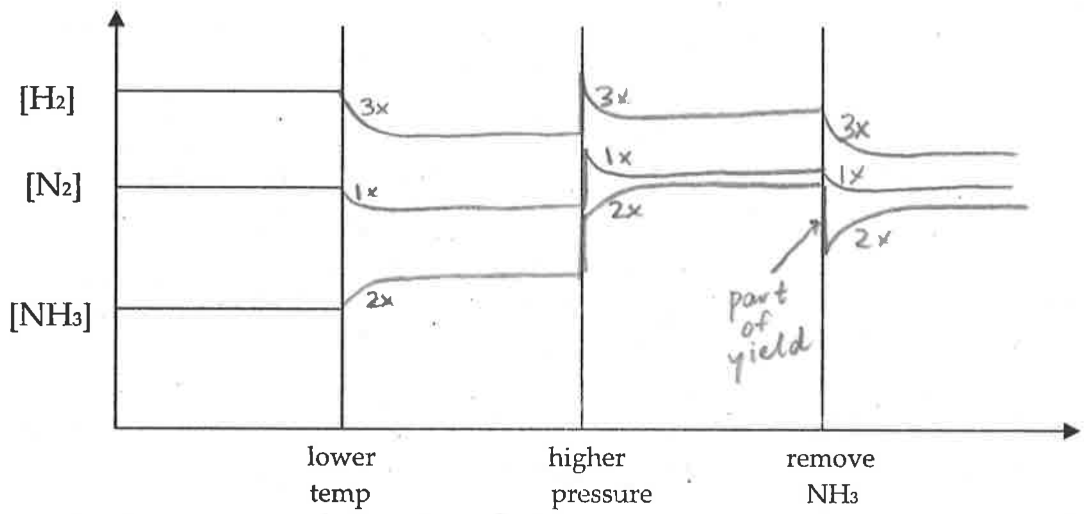
Problems with associated with these conditions:

Low temp. = slow rxn rates * COMPROMISE ⇒ medium temp. (200-400°C)

HIGH pressure = expensive equipment required

What are two other things Haber did to maximize NH_3 production?

- Added catalyst
- constantly removed NH_3 as it was produced.



Assignment 6: Hebden Read p. 56. Do Questions 29-30.

- QUIZ 2 -

VI) The Equilibrium Constant (K_{eq})

A Keq expression can be created by dividing the [products] by the [reactants] in an equilibrium. The result is a Keq constant (no units required).

e.g. $2HI_{(g)} \Leftrightarrow I_{2(g)} + H_{2(g)}$ $K_{eq} = \frac{[products]}{[reactants]} = \frac{[I_2][H_2]}{[HI]^2}$

If the equilibrium is disturbed, it will eventually return to equilibrium, and though the concentrations of each substance may be different than they originally were, the equilibrium constant value (K_{eq} - the ratio of [products] to [reactants]) will remain the same, UNLESS the disturbance is due to a ___temperature___ change (in which ALL of the concentration changes are ___gradual___).

Effects of Changing Conditions on the Value of K_{eq}:

Change in Concentration: ___no change___
Change in Volume: ___no change___
Change in Pressure: ___no change___
Addition of a Catalyst: ___no change___
Change in Temperature: ___changes Keq (unless $\Delta H = 0$ kJ)___

Because ___solids___ and ___pure liquids___ have constant concentrations, they are not included in the K_{eq} expression. When only one liquid is involved in an equilibrium, it is ___pure___; when two or more liquids are involved, they are ___impure___, and included in the K_{eq} expression. Therefore, only ___gases___, ___aqueous substances___, and ___impure liquids___ are included in a K_{eq} expression.

Write K_{eq} expressions for the following:

a) $2H_{2(g)} + O_{2(g)} \Leftrightarrow 2H_2O_{(g)}$

$$K_{eq} = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

b) $3Sn^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)} \Leftrightarrow Sn_3(PO_4)_{2(s)}$

$$K_{eq} = \frac{1}{[Sn^{2+}]^3[PO_4^{3-}]^2}$$

c) $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

ie. this squared!

d) $2N_{2(g)} + 6H_{2(g)} \Leftrightarrow 4NH_{3(g)}$

* don't reduce; it's how it's written that matters for Keq.

$$K_{eq} = \frac{[NH_3]^4}{[N_2]^2[H_2]^6}$$

e) $CaCO_{3(s)}$ + heat ⇔ $CaO_{(s)} + CO_{2(g)}$ $K_{eq} = \frac{[CO_2]}{1} = [CO_2]$

Would the addition of CO_2 change the value of K_{eq}? NO   Would a pressure change alter the value of K_{eq}? NO
Would a temperature change alter the value of K_{eq}? YES

Stress	Shift	$[CaCO_3]$	$[CaO]$	$[CO_2]$	Fwd. Rate	Rev. Rate
Add $CO_{2(g)}$	L	—	—	↑↓ = —	—↑ = ↑	↑↓ = ↑
Decrease volume	L	—	—	↑↓ = —	—↑ = ↑	↑↓ = ↑
Decrease Pressure	R	—	—	↓↑ = —	—↓ = ↓	↓↑ = ↓
Increase Temperature	R	—	—	—↑ = ↑	↑↓ = ↑	↑↑ = ↑

← K_{eq} changes!

Assignment 7: Write K_{eq} Expressions for the following reactions.

1. $2ICl_{(g)} \Leftrightarrow I_{2(g)} + Cl_{2(g)}$
2. $N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)}$
3. $3O_{2(g)} \Leftrightarrow 2O_{3(g)}$
4. $2Bi^{3+}_{(aq)} + 3H_2S_{(g)} \Leftrightarrow Bi_2S_{3(s)} + 6H^+_{(aq)}$
5. $CaCO_{3(s)} \Leftrightarrow CaO_{(s)} + CO_{2(g)}$
6. $CaC_{2(s)} + 2H_2O_{(g)} \Leftrightarrow C_2H_{2(g)} + Ca(OH)_{2(s)}$
7. $C_6H_{6(l)} + Br_{2(l)} \Leftrightarrow C_6H_5Br_{(l)} + HBr_{(g)}$
8. $Cu_{(s)} + 2Ag^+_{(aq)} \Leftrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
9. $4NH_{3(g)} + 5O_{2(g)} \Leftrightarrow 2H_2O_{(g)} + 4NO_{(g)}$
10. $2H_{2(g)} + O_{2(g)} \Leftrightarrow 2H_2O_{(l)}$
11. $3Sn^{2+}_{(aq)} + 2PO_4^{3-}{}_{(aq)} \Leftrightarrow Sn_3(PO_4)_{2(s)}$
12. $4FeS_{2(s)} + 11O_{2(g)} \Leftrightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$
13. $2Na_{(s)} + 2H_2O_{(l)} \Leftrightarrow 2NaOH_{(s)} + H_{2(g)}$
14. $CaCO_{3(s)} + 2HF_{(g)} \Leftrightarrow CaF_{2(s)} + CO_{2(g)} + H_2O_{(g)}$
15. $4NH_{3(aq)} + O_{2(g)} \Leftrightarrow 2N_2H_{4(g)} + 2H_2O_{(g)}$

Assignment 8: Hebden p. 60 #31, 32, 35 abce

Assignment 7 - Keq Expressions

1. $K_{eq} = \frac{[Cl_2][I_2]}{[ICl]^2}$

2. $K_{eq} = \frac{[NO]^2}{[N_2][O_2]}$

3. $K_{eq} = \frac{[O_3]^2}{[O_2]^3}$

4. $K_{eq} = \frac{[H^+]^6}{[Bi^{3+}]^2[H_2S]^3}$

5. $K_{eq} = [CO_2]$

6. $K_{eq} = \frac{[C_2H_2]}{[H_2O]^2}$

7. $K_{eq} = \frac{[C_6H_5Br][HBr]}{[C_6H_6][Br_2]}$ * impure liquids.

8. $K_{eq} = \frac{[Cu^{2+}]}{[Ag^+]^2}$

9. $K_{eq} = \frac{[H_2O]^2[NO]^4}{[NH_3]^4[O_2]^5}$

10. $K_{eq} = \frac{1}{[H_2]^2[O_2]}$

11. $K_{eq} = \frac{1}{[Sn^{2+}]^3[PO_4^{3-}]^2}$

12. $K_{eq} = \frac{[SO_2]^8}{[O_2]^{11}}$

13. $K_{eq} = \frac{[H_2]}{1} = [H_2]$

14. $K_{eq} = \frac{[CO_2][H_2O]}{[HF]^2}$

15. $K_{eq} = \frac{[N_2H_4]^2[H_2O]^2}{[NH_3]^4[O_2]}$

The Size of the K_{eq} Constant:

If the K_{eq} constant is small (less than 1), there is a LOWER concentration of products compared to reactants

If the K_{eq} constant is large (greater than 1), there is a HIGHER concentration of products compared to reactants

in terms of the 'pooling' of reactants/products

Do the following reactions favour reactants or products?

a) $2HBr_{(g)} \Leftrightarrow H_{2(g)} + Br_{2(g)}$ $K_{eq} = 7.0 \times 10^{-20}$ REACTANTS

b) $C_2H_{4(g)} + H_{2(g)} \Leftrightarrow C_2H_{6(g)}$ $K_{eq} = 1.2 \times 10^{19}$ PRODUCTS

c) $Si_{(s)} + O_{2(g)} \Leftrightarrow SiO_{2(g)}$ $K_{eq} = 2.0 \times 10^{-1}$ REACTANTS

For the following reaction:

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

a) Write the K_{eq} expression. The $K_{eq} = 0.25$

$$K_{eq} = 0.25 = \frac{[HF]^2}{[H_2][F_2]}$$

b) Write the K_{eq} expression and find the K_{eq} for this reaction:

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

$$K_{eq} = \frac{[H_2][F_2]}{[HF]^2} = \frac{1}{0.25} = \boxed{4.0}$$

c) Write the K_{eq} expression and find the K_{eq} for this reaction:

$2H_{2(g)} + 2F_{2(g)} \Leftrightarrow 4HF_{(g)}$

$$K_{eq} = \frac{[HF]^4}{[H_2]^2[F_2]^2} = (0.25)^2 = \boxed{0.063} \left(\frac{1}{16}\right)$$

VII) Temperature and the K_{eq} Constant

Remember: An increase in temperature increases both reaction rates, but increases the endothermic reaction more (ie. an increase in temperature favours the endothermic reaction). A decrease in temperature decreases both reaction rates, but decreases the endothermic reaction more (ie. a decrease in temperature favours the exothermic reaction).

If there is a shift to the right due to temperature change, then the ratio [products]/[reactants] will increase and therefore the K_{eq} will increase.

If there is a shift to the left due to a temperature change, then the ratio [products]/[reactants] will decrease and therefore the K_{eq} will decrease.

If the temperature is decreased in the following system, will K_{eq} increase or decrease? Explain.

$$2HI_{(g)} \Leftrightarrow H_{2(g)} + I_{2(g)} \quad \Delta H = +500\ kJ$$

temp. ↓ ⇒ both rates ↓ ⇒ endo (fwd.) ↓ more ⇒ reverse rate faster ⇒ shift (L) ⇒ $\frac{[P]}{[R]}$ ↓ ⇒ K_{eq} ↓

Given the following equation and data:

$$XY + ZM \Leftrightarrow YM + XZ$$

$K_{eq} = 60.0$ at 300°C

$K_{eq} = 45.0$ at 500°C

Is the forward reaction endothermic or exothermic? Explain.

↑ temp ⇒ ↓ K_{eq} ⇒ ↓ $\frac{[P]}{[R]}$ ⇒ shift (L) ⇒ reverse faster.

↑ temp ⇒ both rates ↑ ⇒ endo. ↑ more ⇒ reverse is endo

∴ fwd. rxn is EXOTHERMIC

Assignment 9: Temperature and K_{eq} Exercises

1. Given the following equation and data:

   $$CB + R \Leftrightarrow CBR$$
   $K_{eq} = 12.0$ at 200°C
   $K_{eq} = 20.0$ at 300°C

   Is the forward reaction exothermic or endothermic? Support your answer with explanations.

   ↑ temp. ⇒ ↑ K_{eq} ⇒ ↑ $\frac{[P]}{[R]}$ ⇒ shift (R) → fwd. faster
   ↑ temp. ⇒ ↑ both rates ⇒ ↑ endo more ← fwd. is endothermic

2. Given the following equation and data:

   $$CH_{4(g)} + 2H_2S_{(g)} \Leftrightarrow CS_{2(g)} + 4H_{2(g)}$$
   $K_{eq} = 1.0 \times 10^{-2}$ at 500°C
   $K_{eq} = 2.4 \times 10^{-3}$ at 800°C

a) Is the forward reaction endothermic or exothermic? Explain.

   ↑ temp ⇒ ↓ K_{eq} ⇒ ↓ $\frac{[P]}{[R]}$ ⇒ shift (L) ⇒ reverse faster
   ↑ temp. ⇒ both rates ↑ ⇒ endo ↑ more ← reverse is endo
   ∴ fwd. is exothermic

b) What effect will increasing the $[H_2S]$ have on the value of K_{eq}?

   NONE (only temp. changes affect K_{eq}).

3. For the following reaction:

   $$CO_{2(g)} + H_{2(g)} \Leftrightarrow CO_{(g)} + H_2O_{(g)} \qquad \Delta H = -96 \text{ kJ}$$

   What effect will decreasing the temperature have on the value of K_{eq}? Support your answer with explanations.

↓ temp. ⇒ both rates ↓ ⇒ endo (reverse) ↓ more ⇒ forward faster ⇒ shift (R) ⇒ $\frac{[P]}{[R]}$ ↑ ⇒ K_{eq} ↑.

Assignment 10: Hebden p. 62 #36-41 and #44-46

– QUIZ 3 –

VIII) Type I K_{eq} Problems

1. For the following reaction:

   $2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)}$

   Equilibrium concentrations were measured to be as follows:

   $[SO_2] = 2.0M$, $[O_2] = 0.50M$, $[SO_3] = 1.6M$

   Calculate the value of K_{eq}.

$$K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.6)^2}{(2.0)^2(0.50)} = \boxed{1.3}$$

no units!

2. A 2.00L vessel at equilibrium contained 0.750mol CO, 0.276mol H_2O, 0.600mol CO_2, and a $K_{eq} = 0.986$. Calculate the moles of H_2 at equilibrium.

   $CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$

$$[CO] = \frac{mol}{V} = \frac{0.750\ mol}{2.00\ L} = 0.375\ M\ CO \qquad [CO_2] = \frac{0.600\ mol}{2.00\ L} = 0.300\ M\ CO_2$$

$$[H_2O] = \frac{0.276\ mol}{2.00\ L} = 0.138\ M\ H_2O$$

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$[H_2] = \frac{K_{eq}[CO][H_2O]}{[CO_2]} = \frac{(0.986)(0.375\ M)(0.138\ M)}{0.300\ M}$$

$$= 0.17\underline{0}1\ M$$

$$mol = MV = (0.17\underline{0}1\ M)(2.00\ L) = \boxed{0.340\ mol\ H_2}$$

Assignment 11: Type I Problems

1. For the following reaction at equilibrium:

$$CH_{4(g)} + H_2O_{(g)} \Leftrightarrow CO_{(g)} + 3H_{2(g)}$$

   $[CH_4] = 0.600M$ $[H_2O] = 0.060M$
   $[CO] = 0.200M$ $[H_2] = 0.700M$
   Calculate the K_{eq} for this reaction. Are the reactants or products favoured?

2. For the following reaction at equilibrium:

$$A_{2(g)} + B_{(l)} \Leftrightarrow A_{(g)} + AB_{(g)}$$

   a) Write the equilibrium expression.
   b) Calculate the [A] if $K_{eq} = 1.5 \times 10^{-3}$, $[A_2] = 2.5 \times 10^{-4}M$ and $[AB] = 1.2 \times 10^{-4}M$.
   c) Predict the effect of removing some $AB_{(g)}$ on the value of K_{eq}.
   d) For this reaction, are the reactants or products favoured?

3. For the following reaction:

$$CO_{(g)} + H_2O_{(l)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$$

   At equilibrium in a 1.0L container, 0.020mol of CO, 0.010mol H_2O, 0.030 mol CO_2, and 0.010mol of H_2 are present.
   Calculate the K_{eq} and state whether reactants or products are favoured.

4. For the following reaction:

$$CO_{(g)} + 2H_{2(g)} \Leftrightarrow CH_3OH_{(g)} \qquad K_{eq} = 1.00$$

   At equilibrium in a 2.0L container, 0.420mol CO and 0.100mol H_2 are present. Calculate the number of moles of CH_3OH present.

5. A 4.00L flask contains 6.00mol $NO_{2(g)}$, 3.0mol $NO_{(g)}$, and 4.0mol of $O_{2(g)}$ at equilibrium. Write a balanced equation and calculate the K_{eq} for the reaction in which NO reacts with O_2 to produce NO_2.

6. Consider the following reaction:

$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

An equilibrium mixture of these gases in a 2.0L container contains 0.10M NH_3, 0.440M N_2, and 0.080M H_2. What is the K_{eq} ?

7. For the following reaction at equilibrium and data:

$N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

	$[N_2]_{eq}$ (M)	$[H_2]_{eq}$ (M)	$[NH_3]_{eq}$ (M)
Trial 1	0.200	0.400	0.500
Trial 2	?	0.300	0.600

Find $[N_2]$ in Trial 2.

8. Do Hebden p. 71 #56.

IX) Type II K_{eq} Problems

1. At a certain temperature, a mixture of H_2 and I_2 was prepared by placing 0.100mol of H_2 and 0.100mol of I_2 into a 1.00L flask. At equilibrium, the I_2 concentration dropped to 0.020M. Calculate the K_{eq}.

mol = M (1.0 L container)
* careful w/ sigfigs!

	$H_{2(g)}$	+ $I_{2(g)}$	$\Leftrightarrow$ $2HI_{(g)}$
Initial	0.100 M	0.100 M	0 M
Change	− 0.080 M	− 0.080 M	+ 0.16 M
Equilibrium	0.020 M	0.020 M	0.16 M

* stoichiometry governs the 'change'!

$$K_{eq} = \frac{[HI]_{eq}^2}{[H_2]_{eq}[I_2]_{eq}} = \frac{(0.16)^2}{(0.020)^2} = \boxed{64}$$

Assignment 11: Type I Problems

1. $K_{eq} = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{(0.200)(0.700)^3}{(0.600)(0.060)} = \boxed{1.9}$ $1.9 > 1$ ∴ PRODUCTS FAVOURED.

2. a) $K_{eq} = \frac{[A][AB]}{[A_2]}$ b) $[A] = \frac{(K_{eq})[A_2]}{[AB]} = \frac{(1.5\times10^{-3})(2.5\times10^{-4}M)}{1.2\times10^{-4}}$ $\boxed{[A] = 3.1\times10^{-3}\ M}$

c) NO EFFECT d) $1.5\times10^{-3} < 1$ ∴ REACTANTS FAVOURED

3. mol = M (due to 1.0 L container).

$K_{eq} = \frac{[CO_2][H_2]}{[CO]} = \frac{(0.030)(0.010)}{0.020} = \boxed{1.5\times10^{-2}}$ REACTANTS FAVOURED

4. $[CO] = \frac{0.420\ mol}{2.0\ L} = 0.210\ M$ $[H_2] = \frac{0.100\ mol}{2.0\ L} = 0.050\ M$

$K_{eq} = \frac{[CH_3OH]}{[CO][H_2]^2} \longrightarrow [CH_3OH] = (K_{eq})[CO][H_2]^2$

$= (1.00)(0.210)(0.050)^2$

$= 5.25\times10^{-4}\ M$

mol CH_3OH = MV = $(5.25\times10^{-4}\ M)(2.0\ L) = \boxed{1.1\times10^{-3}\ mol}$

5. $[NO_2] = \frac{6.00\ mol}{4.00\ L} = 1.50\ M$ $[NO] = \frac{3.00\ mol}{4.00\ L} = 0.75\ M$ $[O_2] = \frac{4.0\ mol}{4.00\ L} = 1.0\ M$

$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_2$ $K_{eq} = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(1.50)^2}{(0.75)^2(1.0)} = \boxed{4.0}$

6. $K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.10)^2}{(0.440)(0.080)^3} = \boxed{44}$

7. No temp. change so K_{eq} remains unchanged!

Trial 1: $K_{eq} = \frac{(0.500)^2}{(0.200)(0.400)^3} = 19.531$

Trial 2: $19.531 = \frac{(0.600)^2}{[N_2](0.300)^3}$ $[N_2]$ (trial 2) = $\boxed{0.683\ M}$

2. $N_{2(g)} + 3H_{2(g)} \Leftrightarrow 2NH_{3(g)}$

Given: $[N_2]_i = 0.32M$

$[H_2]_i = 0.66M$

$[NH_3]_i = 0M$

$[H_2]_{eq} = 0.30M$

Calculate the value of K_{eq}.

	$N_{2(g)}$ +	$3H_{2(g)}$ ⇔	$2NH_{3(g)}$
I	0.32M	0.66 M	0 M
C	−0.12 M	−0.36 M	+0.24 M
E	0.20 M	0.30 M	0.24 M

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.24)^2}{(0.20)(0.30)^3} = 10.67 = \boxed{11}$$

Assignment 12: Type II Exercises; Also do pp. 70-71 Qs 47-49, 57.

1. 0.0740mol of $PCl_{5(g)}$ was introduced into a 1.00L container and allowed to come to equilibrium.

$$PCl_{5(g)} \Leftrightarrow PCl_{3(g)} + Cl_{2(g)}$$

At equilibrium, the $[PCl_3] = 0.0500M$

a) What is the value of K_{eq} for this reaction?

b) What is the equilibrium $[Cl_2]$ and $[PCl_5]$?

2. A mixture consisting of 1.00mol $CO_{(g)}$ and 1.00mol $H_2O_{(g)}$ is placed in a 10.00L container. At equilibrium, 0.665mol $CO_{2(g)}$ and 0.665mol $H_{2(g)}$ are present.

$$CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$$

Calculate the K_{eq} for this reaction.

3. When 1.00mol of HBr is placed in a 1.00L flask, the following equilibrium is achieved:

$$2HBr_{(g)} \Leftrightarrow H_{2(g)} + Br_{2(g)}$$

At equilibrium, 0.140mol of H_2 is present. Calculate the K_{eq}.

4. A 5.00L vessel was initially filled with 6.00mol SO_2, 2.50mol NO_2, and 1.00mol SO_3.

$$SO_{2(g)} + NO_{2(g)} \Leftrightarrow SO_{3(g)} + NO_{(g)}$$

At equilibrium, the vessel was found to contain 3.00mol SO_3. What is the K_{eq} for the reaction?

5. 0.50mol of NOCl was introduced into a 1.0L flask and allowed to come to equilibrium:

$$2NOCl_{(g)} \Leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$

At equilibrium, there was 0.10mol of Cl_2. What is the K_{eq} ?

- QUIZ 4 -

X) Type III K_{eq} Problems

1. $$H_{2(g)} + I_{2(g)} \Leftrightarrow 2HI_{(g)} \qquad K_{eq} = 55.6$$

$[H_2]_i = 0.200M$, $[I_2]_i = 0.200M$

What is the equilibrium [HI]?

Let $x = \Delta[H_2]$

	$H_{2(g)}$ +	$I_{2(g)}$ ⇔	$2HI_{(g)}$
I	0.200 M	0.200 M	0 M
C	$-x$	$-x$	$+2x$
E	$0.200-x$	$0.200-x$	$2x$

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} \Rightarrow 55.6 = \frac{(2x)^2}{(0.200-x)^2}$$

$$7.45654 = \frac{2x}{0.200-x}$$

$$1.49131 = 9.45654x$$

$$x = 0.157701$$

$$[HI] = 2x = \boxed{0.315\,M}$$

Assignment 12 - Type II Exercises

1. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ mol = M (1.0 L container)

	PCl_5	PCl_3	Cl_2
I	0.0740 M	0	0
C	−0.0500	+0.0500	+0.0500
E	0.0240	0.0500 M	0.0500 M

a) $K_{eq} = \frac{(0.0500)(0.0500)}{0.0240} = \boxed{0.104 = 1.04 \times 10^{-1}}$

b) $[Cl_2]_{eq} = 0.0500\ M$ $[PCl_5]_{eq} = 0.0240\ M$

2. $[CO] = \frac{1.00\ mol}{10.00\ L} = 0.100\ M$ $[H_2O] = \frac{1.00\ mol}{10.00\ L} = 0.100\ M$ $[CO_2]_{eq} = \frac{0.665\ mol}{10.00\ L} = 0.0665\ M$

$[H_2]_{eq} = \frac{0.665\ mol}{10.00\ L} = 0.0665\ M$

$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$

	CO	H_2O	CO_2	H_2
I	0.100 M	0.100 M	0	0
C	−0.0665	−0.0665	+0.0665	+0.0665
E	0.0335	0.0335	0.0665 M	0.0665 M

← 2 sig figs

$K_{eq} = \frac{(0.0665)^2}{(0.0335)^2} = \boxed{3.9}$

3. mol = M (1.0 L container)

$2HBr_{(g)} \rightleftharpoons H_{2(g)} + Br_{2(g)}$

	HBr	H_2	Br_2
I	1.00 M	0	0
C	−0.280	+0.140	+0.140
E	0.72 M	0.140 M	0.140 M

$K_{eq} = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(0.140)^2}{(0.72)^2} = \boxed{0.038}$

4. $[SO_2] = \frac{6.00\ mol}{5.00\ L} = 1.20\ M$ $[NO_2] = \frac{2.50\ mol}{5.00\ L} = 0.500\ M$ $[SO_3]_i = \frac{1.00\ mol}{5.00\ L} = 0.200\ M$

$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$ $[SO_3]_{eq} = \frac{3.00\ mol}{5.00\ L} = 0.600\ M$

	SO_2	NO_2	SO_3	NO
I	1.20 M	0.500 M	0.200 M	0 M
C	−0.400 M	−0.400 M	+0.400	+0.400
E	0.80 M	0.100 M	0.600 M	0.400 M

$K_{eq} = \frac{(0.600)(0.400)}{(0.80)(0.100)} = \boxed{3.0}$

5. mol = M (1.0 L container) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

	$NOCl$	NO	Cl_2
I	0.50 M	0	0
C	−0.20 M	+0.20	+0.10
E	0.30 M	0.20 M	0.10 M

$K_{eq} = \frac{(0.10)(0.20)^2}{(0.30)^2} = \boxed{4.4 \times 10^{-2}}$

2. $CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)}$ $K_{eq} = 4.06$

$[CO]_i = 0.10M$, $[H_2O]_i = 0.10M$

What are the equilibrium concentrations of all species?

Let $x = \Delta[CO]$

	$CO_{(g)}$	+ $H_2O_{(g)}$	$\Leftrightarrow$ $CO_{2(g)}$	+ $H_{2(g)}$
I	0.10 M	0.10 M	0 M	0 M
C	$-x$	$-x$	$+x$	$+x$
E	$0.10-x$	$0.10-x$	x	x

$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} \Rightarrow 4.06 = \frac{x^2}{(0.10-x)^2} \Rightarrow 2.0149 = \frac{x}{0.10-x}$$

$$0.20149 = 3.0149x$$

$$x = 0.06683$$

$[CO_2] = [H_2] = 0.067M$

$[CO] = [H_2O] = 0.10 M - 0.06683M = 0.03317 M$

$= 0.03M$

3. A certain amount of H_2O was placed in a 2.00L closed flask. When equilibrium was reached, the $[H_2]$ was 0.500M. If $K_{eq} = 16.0$ at this temperature, how many moles of H_2O were originally placed in the flask?

Let $x = [H_2O]_i$

	$2H_2O_{(g)}$	$\Leftrightarrow$ $2H_{2(g)}$	+ $O_{2(g)}$
I	x	0	0
C	$-0.500M$	$+0.500M$	$+0.250M$
E	$x-0.500M$	$0.500M$	$0.250M$

$$K_{eq} = 16.0 = \frac{[H_2]^2[O_2]}{[H_2O]^2} \Rightarrow 16.0 = \frac{(0.500)^2(0.250)}{x-0.500}$$

$$(x-0.500)^2 = \frac{(0.500)^2(0.250)}{16.0} \Rightarrow (x-0.500)^2 = 0.00390625$$

$$x - 0.500 = 0.0625$$

$$x = [H_2O]_i = 0.5625 M$$

$$mol = MV = (0.5625M)(2.00L) = 1.13 \text{ mol } H_2O_i$$

Assignment 13: Type III Exercises; Also do p71-72 Qs 52-53, 58, 60-66

1. For the following reaction:

   $H_{2(g)} + CO_{2(g)} \Leftrightarrow H_2O_{(g)} + CO_{(g)}$ $K_{eq} = 0.771$

   If 0.0100mol of H_2 and 0.0100mol of CO_2 are mixed in a 1.00L container, what are the concentrations of all substances at equilibrium?

2. For the following reaction:

   $2IBr_{(g)} \Leftrightarrow I_{2(g)} + Br_{2(g)}$ $K_{eq} = 8.5 \times 10^{-3}$

   If 0.0600mol of IBr is placed in a 1.0L container, what are the concentrations of all three substances at equilibrium?

3. For the following reaction:

   $FeO_{(s)} + CO_{(g)} \Leftrightarrow Fe_{(s)} + CO_{2(g)}$ $K_{eq} = 0.403$

   If 0.0500mol of CO and excess solid FeO are placed in a 1.00L container, what are the concentrations of CO and CO_2 when equilibrium has been attained?

4. For the following reaction:

   $2HCl_{(g)} \Leftrightarrow H_{2(g)} + Cl_{2(g)}$ $K_{eq} = 4.00$

   An unknown [HCl] was added to a 2.00L flask and allowed to reach equilibrium. At equilibrium, $[H_2] = 0.200M$. How many moles of HCl was originally placed in the flask?

5. For the following reaction:

   $N_2O_{2(g)} + H_{2(g)} \Leftrightarrow N_2O_{(g)} + H_2O_{(g)}$ $K_{eq} = 1.00$

   If 0.150mol each of N_2O and H_2O are introduced into a 1.00L flask and allowed to come to equilibrium, what concentration of N_2O_2 will be present at equilibrium?

Assignment 13 - Type III Exercises

1. mol = M (1.0 L container)

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

Let $x = \Delta[CO]$

	H_2	CO_2	H_2O	CO
I	0.0100 M	0.0100 M	0	0
C	$-x$	$-x$	$+x$	$+x$
E	$0.0100-x$	$0.0100-x$	x	x

$K_{eq} = 0.771$

$$K_{eq} = \frac{[H_2O][CO]}{[H_2][CO_2]} \Rightarrow 0.771 = \frac{x^2}{(0.0100-x)^2} \Rightarrow x = 0.004675\text{ M}$$

$[H_2] = [CO_2] = 0.0100 - 0.004675 =$ **0.0053 M**

$[H_2O] = [CO] =$ **0.00468 M**

2. mol = M (1.0 L container)

$$2IBr_{(g)} \rightleftharpoons I_{2(g)} + Br_{2(g)} \qquad K_{eq} = 8.5 \times 10^{-3}$$

	IBr	I_2	Br_2
I	0.060 M	0	0
C	$-2x$	$+x$	$+x$
E	$0.060-2x$	x	x

Let $x = \Delta[I_2]$

$$K_{eq} = \frac{[I_2][Br_2]}{[IBr]^2} \Rightarrow \frac{x^2}{(0.060-2x)^2} = 8.5 \times 10^{-3} \Rightarrow \frac{x}{0.060-2x} = 0.092195$$

$x = 4.671 \times 10^{-3}$ M

$[I_2] = [Br_2] =$ **4.7×10^{-3} M**

$[IBr] = 0.060 - 2(0.004671) = 0.05066\text{ M} =$ **0.051 M**

3. mol = M (1.00 L container)

$$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)} \qquad K_{eq} = 0.403$$

	CO	CO_2
I	0.0500 M	0 M
C	$-x$	$+x$
E	$0.0500-x$	x

Let $x = \Delta[CO_2]$

$$K_{eq} = \frac{[CO_2]}{[CO]} \Rightarrow 0.403 = \frac{x}{0.0500-x} \Rightarrow x = 0.014362\text{ M}$$

$[CO_2] = 1.44 \times 10^{-2}\text{ M} =$ **0.0144 M**

$[CO] = 0.0500 - 0.014362 =$ **0.0356 M**

4. $2HCl_{(g)} \rightleftharpoons H_{2(g)} + Cl_{2(g)}$ $K_{eq} = 4.00$

	$2HCl_{(g)}$	$H_{2(g)}$	$Cl_{2(g)}$
I	x	0	0
C	$-0.400M$	$+0.200M$	$+0.200M$
E	$(x-0.400)M$	$0.200M$	$0.200M$

Let $x = [HCl]_i$

$$K_{eq} = \frac{[H_2][Cl_2]}{[HCl]^2} \Rightarrow 4.00 = \frac{(0.200)^2}{(x-0.400)^2} \Rightarrow 2.00 = \frac{0.200}{x-0.400}$$

$x = 0.500\text{ M}$

$[HCl]_i = 0.500M$

mol HCl = $MV = (0.500M)(2.00L) =$ **1.00 mol**

5. mol = M (1.00 L container)

$N_2O_{2(g)} + H_{2(g)} \rightleftharpoons N_2O_{(g)} + H_2O_{(g)}$ $K_{eq} = 1.00$

	$N_2O_{2(g)}$	$H_{2(g)}$	$N_2O_{(g)}$	$H_2O_{(g)}$
I	0	0	0.150 M	0.150 M
C	$+x$	$+x$	$-x$	$-x$
E	x	x	$0.150-x$	$0.150-x$

Let $x = \Delta[H_2]$

Two ways to solve: (same answer)

① Equation given as above

$$K_{eq} = \frac{[N_2O][H_2O]}{[N_2O_2][H_2]} \Rightarrow 1.00 = \frac{(0.150-x)^2}{x^2}$$

$x = 0.0750\text{ M}$

$[N_2O_2] =$ **0.0750 M**

② N_2O & H_2O are <u>reactants</u> ∴ reverse eq'n and take <u>reciprocal</u> of K_{eq} (which, in this case, is still 1.00)

$$K_{eq} = \frac{[N_2O_2][H_2]}{[N_2O][H_2O]} \Rightarrow 1.00 = \frac{x^2}{(0.150-x)^2}$$

$x = 0.0750\text{ M}$

$[N_2O_2] =$ **0.0750 M**

* if $K_{eq} \neq 1$, then how you write the expression dictates K_{eq}'s value.

XI) Type IV K_{eq} Problems

These problems use a TRIAL K_{eq} ('Q' in Hebden), which is used to test if the present ('person-made') conditions indicate the existence of an equilibrium, or if a shift in a certain direction still has to occur for the reaction to attain equilibrium. If a shift must occur, the relative magnitude of the TRIAL K_{eq}, compared to the actual K_{eq}, can be used to determine whether the shift will be to the right or to the left.

1. Is the following reaction at equilibrium? If not, in which direction must the reaction shift to reach equilibrium?

$$CO_{(g)} + H_2O_{(g)} \Leftrightarrow CO_{2(g)} + H_{2(g)} \qquad K_{eq} = 10.0$$

0.80M 0.050M 0.50M 0.40M

$$\text{Trial } K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.50)(0.40)}{(0.80)(0.050)} = 5.0$$ not at equilibrium! ($5.0 \neq 10.0$)

Trial $K_{eq} < K_{eq} \Rightarrow \frac{[P]_i}{[R]_i} < \frac{[P]_{eq}}{[R]_{eq}} \Rightarrow$ rxn must shift (R) to reach equil. (fwd. faster).

2. The following reaction occurs in a 2.0L container:

$$Br_{2(g)} + Cl_{2(g)} \Leftrightarrow 2BrCl_{(g)} \qquad K_{eq} = 3.2 \times 10^{-2}$$

Quantities of gases were found to be as follows:

$Br_2 = 0.60$ mol, $Cl_2 = 0.80$ mol, $BrCl = 2.20$ mol

What will happen to the $[Br_2]$ as the system approaches equilibrium?

$[Br_2] = \frac{0.60 \text{ mol}}{2.0 \text{ L}} = 0.30 \text{ M}$

$[Cl_2] = \frac{0.80 \text{ mol}}{2.0 \text{ L}} = 0.40 \text{ M}$

$[BrCl] = \frac{2.20 \text{ mol}}{2.0 \text{ L}} = 1.1 \text{ M}$

$$\text{Trial } K_{eq} = \frac{[BrCl]^2}{[Br_2][Cl_2]} = \frac{(1.1)^2}{(0.30)(0.40)} = 10.1$$

Trial $K_{eq} > K_{eq}$ $\left(\frac{[P]_i}{[R]_i}\right) > \left(\frac{[P]_{eq}}{[R]_{eq}}\right) \Rightarrow$ rxn must shift (L) to attain equil. (rev. faster)

$[Br_2] \uparrow$

Assignment 14: Type IV Exercises; Also do p70-71 Qs 50bc, 51bc, 54.

- QUIZ 5 -

1. For the following reaction:

$$2HF_{(g)} \Leftrightarrow H_{2(g)} + F_{2(g)} \qquad K_{eq} = 4.0$$

Predict the direction in which the equilibrium will shift when the following systems are introduced into a 5.0L vessel.

a) 3.0mol HF, 2.0mol H_2, and 4.0mol F_2

b) 0.20mol HF, 0.50mol H_2, and 0.60mol F_2

c) 0.30mol HF, 1.8mol H_2, and 0.20mol F_2

2. For the following reaction:

$$2O_{3(g)} \Leftrightarrow 3O_{2(g)} \qquad K_{eq} = 75$$

Predict the direction in which the equilibrium will shift, if any, when the following substances are introduced into a 10.0L container?

a) 0.60mol O_3 and 3.0mol O_2

b) 0.050mol O_3 and 7.0mol O_2

c) 1.5mol O_3 and 0.20mol O_2

3. For the following reaction:

$$H_{2(g)} + Cl_{2(g)} \Leftrightarrow 2HCl_{(g)} \qquad K_{eq} = 0.15$$

Equal moles of each of the three gases are in a 1.0L vessel. What direction will the reaction shift in order to reach equilibrium?

4. Consider the following reaction:

$$2SO_{2(g)} + O_{2(g)} \Leftrightarrow 2SO_{3(g)} \qquad K_{eq} = 75$$

A student places 0.50moles SO_2, 0.080mol O_2, and 1.0mol SO_3 into a 1.0L flask. The student predicts that the $[SO_2]$ will decrease as equilibrium is established. Do you agree with the student's prediction? Explain using appropriate calculations.

5. Consider the following reaction:

$$2C_{(s)} + O_{2(g)} \Leftrightarrow 2CO_{(g)} \qquad K_{eq} = 1.20 \times 10^{-2}$$

If 2.0mol C, 0.800mol O_2, and 0.600mol CO are placed into a 1.0L flask, in which direction will the equilibrium shift in order to achieve equilibrium? What will happen to the [C]? Show all calculations.

6. Type III & Type IV hybrid question ☺

Consider the following reaction:

$$N_{2(g)} + O_{2(g)} \Leftrightarrow 2NO_{(g)} \qquad K_{eq} = 1.20 \times 10^{-4}$$

If 0.060mol N_2, 0.060mol O_2, and 0.00025mol NO are mixed in a 1.0L container, in which direction will the reaction proceed in order to achieve equilibrium? What will be the equilibrium [N_2], [O_2], and [NO] ?

Assignment 14 - Type IV Exercises

1. $2\,HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$ $K_{eq} = 4.0$ Trial $K_{eq} = \frac{[H_2][F_2]}{[HF]^2}$

a) $[HF] = 0.6\,M$ $[H_2] = 0.4\,M$ $[F_2] = 0.8\,M$

Trial $K_{eq} = 0.89 < K_{eq}$

Rxn shifts RIGHT to attain equil.

b) $[HF] = 0.040\,M$ $[H_2] = 0.10\,M$ $[F_2] = 0.12\,M$

Trial $K_{eq} = 7.5 > K_{eq}$

Rxn shifts LEFT to attain equil.

c) $[HF] = 0.060\,M$ $[H_2] = 0.36\,M$ $[F_2] = 0.040\,M$

Trial $K_{eq} = 4.0 = K_{eq}$

Rxn is AT equilibrium! (no shift req'd!)

2. $2\,O_{3(g)} \rightleftharpoons 3\,O_{2(g)}$ $K_{eq} = 75$ Trial $K_{eq} = \frac{[O_2]^3}{[O_3]^2}$

a) $[O_3] = 0.060\,M$ $[O_2] = 0.30\,M$

Trial $K_{eq} = 7.5 < K_{eq}$

Rxn shifts RIGHT to attain equilibrium.

b) $[O_3] = 0.0050\,M$ $[O_2] = 0.70\,M$

Trial $K_{eq} = 13720 > K_{eq}$

Rxn shifts LEFT to attain equil.

c) $[O_3] = 0.15\,M$ $[O_2] = 0.020\,M$

Trial $K_{eq} = 3.56 \times 10^{-4} < K_{eq}$

Rxn shifts RIGHT to attain equil.

3. $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2\,HCl_{(g)}$ $K_{eq} = 0.15$

Assume x mol of each substance. (mol = M (1.0 L container)).

Trial $K_{eq} = \frac{[HCl]^2}{[H_2][Cl_2]} = \frac{x^2}{x^2} = 1 > K_{eq}$ Rxn will shift LEFT to attain equil.

4. $2\,SO_{2(g)} + O_{2(g)} \rightleftharpoons 2\,SO_{3(g)}$ $K_{eq} = 75$

mol = M (1.0 L container)

Trial $K_{eq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(1.0)^2}{(0.50)^2(0.080)} = 50 < K_{eq}$ Rxn will shift RIGHT to attain equil.

$[SO_2] \downarrow$ ∴ STUDENT is CORRECT!

5. $2\,C_{(s)} + O_{2(g)} \rightleftharpoons 2\,CO_{(g)}$ $K_{eq} = 1.20 \times 10^{-2}$

mol = M (1.0 L container)

$$\text{Trial } K_{eq} = \frac{[CO]^2}{[O_2]} = \frac{(0.600)^2}{0.800} = 0.45 > K_{eq}$$

Rxn will shift LEFT to attain equil.

$[C_{(s)}]$ will not change but the AMOUNT of $C_{(s)}$ will increase!

6. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{(g)}$ $K_{eq} = 1.20 \times 10^{-4}$

mol = M (1.0 L container)

$$\text{Trial } K_{eq} = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2.5 \times 10^{-4})^2}{(0.060)(0.060)} = 1.736 \times 10^{-5} < K_{eq}$$

Rxn will shift RIGHT to attain equil.

	$N_{2(g)}$	+ $O_{2(g)}$	$\rightleftharpoons$ $2\,NO_{(g)}$
I	0.060 M	0.060 M	2.5×10^{-4} M
C	$-x$	$-x$	$+2x$
E	$0.060-x$	$0.060-x$	$2.5 \times 10^{-4} + 2x$

let $x = \Delta[N_2]$

$$K_{eq} = 1.20 \times 10^{-4} = \frac{(2.5 \times 10^{-4} + 2x)^2}{(0.060-x)^2}$$

$$0.010954 = \frac{2.5 \times 10^{-4} + 2x}{0.060 - x}$$

$$x = 0.0002025 \text{ M}$$

$[N_2] = [O_2] = 0.060 - 0.000252$ $= \boxed{0.060 \text{ M}}$

$[NO] = \boxed{6.6 \times 10^{-4} \text{ M}}$