Equilibrium

Examples of Different Equilibria

K_p	H_2 +	N_2 ⇔	NH_3	
K_a	$HC_2H_3O_2$	⇔	H^+	+ $C_2H_3O_2^-$
K_{sp}	$SrCrO_4$	⇔	Sr^{2+}	+ CrO_4^{2-}

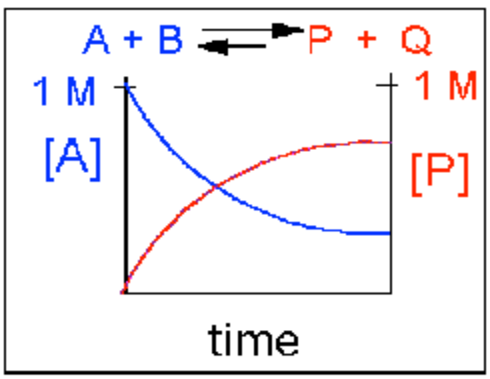
Equilibrium deals with: What is the balance between products and reactants?

Reversible Reaction Plot - arrows in both directions

A (g) (blue) + B (g) ⇔ P (red) + Q (g)

Forward →

← Reverse



http://employees.csbsju.edu/hjakubowski/classes/ch111/olsg-ch111/equilibkinetics/equilbkin.htm

After some time, chemical equilibrium is established.
Rate forward and rate reverse are equal.
Dynamic equilibrium because changes still occur.

Equilibrium for one step mechanism

A_2 + B_2 ⇔ 2 AB

Rate forward = $k_f [A_2] [B_2]$
Rate reverse = $k_r [AB]^2$

At equilibrium

Rate forward = Rate reverse

$k_f [A_2] [B_2] = k_r [AB]^2$

$$K = (k_f / k_r) = \{[AB]^2 / [A_2][B_2]\} = \frac{\text{Products}}{\text{Reactants}}$$

K= equilibrium constant
K has different value for every reaction and changes with temperature

Equilbrium – in general

For any reaction that is reversible (reactants to products and products to reactants)

$$aA + bB \Leftrightarrow cC + dD$$

Expression for Equilibrium constant

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

Note: Coefficients become exponents since there may be more than one of a species.

Example:

$$2NO_2Cl \Leftrightarrow 2NO_2 + Cl_2$$

$$K = \frac{[NO_2]^2 [Cl_2]}{[NO_2Cl]^2}$$

think of K as ratio of products over reactants (products/reactants)

Can go from Balanced Equation to Equilibrium Constant Expression.

Heterogeneous Equilibria

(gas) (solid) (liquid) (dissolved molecule in solution)

Concentration of pure liquid and pure solid is equal to 1 "one" so **do not include pure solid or pure liquid** in equilibrium expression. Only include gases and dissolved species that are in solution.

Summary of Rules for Equilibrium constants expressions

1. Products go in numerator (top)   Reactants go in denominator(bottom)
2. Don't include pure solid or pure liquid (only gases or concentration of chemical species dissovled)
3. K varies with temperature (can increase or decrease as T raised)
4. "Large K favors products" (more products than reactants)
   "Small K favors reactants" (more reactants than products)

Problems using Equilibrium Constants

1) Given concentrations at equilibrium find K.
Example
Given the reaction and equilibrium concentrations below, find K:

$N_2O_4 \Leftrightarrow 2NO_2\ (g)$

$[N_2O_4] = 4.3\text{x}10^{-2}$M $[NO_2] = 1.4\text{x}10^{-2}$ M

$K = \frac{[NO_2]^2}{[N2O_4]} = \frac{[1.4\ \text{x}10^{-2}]^2}{[4.3\ \text{x}10^{-2}]} = 4.7\text{x}10^{-3}$ mol/L   Small K so Reactants favored

2) Use K to find conc. of reactants and products at equilibrium.
Example
Given $K = 2.7\text{x}\ 10^{-7}$
and initial amounts of [A]=1.0 [B]=0 and [C]=0
then find concentrations at Equilibrium for reaction

2A	⇔	B	+	3C
1.0		0		0
?		?		?

(a) make table of initial, change, and final in symbolic form

	2A	⇔	B	+	3C
I initial	1.00		0		0
C change	-2x		+x		+3x
E equilibrium (final)	1.00-2x		x		3x

after work below find for equilibrium the value of x

final	1.00-2(.010)	.010	3(.010)
	0.980	.010	.030

below shows how to find value of x (in this case x = 0.010)

(b) write Equilibrium expression and sub in symbols

$K = [B][C]^3/[A]^2 = [x]\ [3x]^3/[1-2x]^2$

(c) sub in for K and solve math exactly or simplify to approximate

$2.7x10^{-7} = 27x^4 / [1-2x]^2$

since K is small then x is small so approximate **1-2x ~ 1**

$2.7x10^{-7} = 27 x^4 / [1]^2$
$1.0 x10^{-8} = x^4$
$(1.0 x10^{-8})^{1/4} = (x^4)^{1/4}$
$1.0 x 10^{-2} = x$

(d) Test solution by substituting back in for x

$K= [x][3x]^3/[1-2x]^2$
$= [1x10^{-2}] [3(1x10^{-2})]^3/[1- 2(1x10^{-2})]^2$
$= [0.01][0.03]^3 / [0.98]^2$
$= 2.8x10^{-7}$

This K is off by about 4% from $K=2.7x10^{-7}$ but close enough to use approximation to avoid more complicated math!

<u>Example - find concentrations from K</u>
Given K and initial concentrations. Find final concentrations.

Given:

$H_2 (g) + CO_2 (g) \Leftrightarrow H_2O (g) + CO (g)$
and K= 0.771 at 750°C
and Initial conc. $[H_2]$ = 0.0100 mol/L $[CO_2]$ = 0.0100 mol/L

a) make table

	H_2 (g)	+ CO_2 (g)	⇔	H_2O (g)	+	CO (g)
initial	0.010	0.010		0		0
change	- x	-x		+x		+x
final	(.010- x)	(.010 –x)		x		x

b) write K expression

$$K= \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{(x)\,(x)}{(.01 - x)\,(.01 - x)} = 0.771$$

c) sub in numbers do math – simplify if possible

Simple approach:

$$x^2 / (0.010 - x)^2 = 0.771$$

square root of both sides

$$x / (0.010-x) = 0.878$$

and solve for x

$$\mathbf{x} = 8.78x10^{-3} - 0.878\,\mathbf{x}$$

$$1.878\,\mathbf{x} = 8.78x10^{-3}$$

$$\mathbf{x} = 4.68\ x10^{-3}$$ approximate value

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

and $[H_2] = [CO_2] = 0.0100 - 0.00468 = 0.00532M$

d) check K value

$$K = \frac{[H_2O]\,[CO]}{[H_2]\,[CO_2]} = \frac{(0.00468)\,(0.00468)}{(0.00532)\,(0.00532)} = 0.774$$

and notice that get a K that agrees closely with original K = 0.77
so approximation okay

Exact Solution for above problem is shown below
using quadratic equation:

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

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

$$K = x^2 / (0.010 - x)^2$$

$$0.77 = x^2 / (0.010 - x)^2$$

$$\mathbf{x}^2 = (0.77)\,(1.0x10^{-4} - 2x10^{-2}\,\mathbf{x} + \mathbf{x}^2)$$

$$-0.23\mathbf{x}^2 - 1.54x10^{-2}\,\mathbf{x} + 7.7 * 10^{-5} = 0$$

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

$$\frac{-(-1.54 * 10^{-2}) \pm \sqrt{((-1.54 * 10^{-2})^2 - 4(-0.23)\,(7.7 * 10^{-5})}}{2\,(-0.22)}$$

$$\frac{-(0.154) \pm 0.01754}{-0.46}$$

x = 0.00467

or -0.0718 (rejected value since cannot have negative conc)

Notice in this case very little difference between
approximate **x** $= 4.68 \times 10^{-3}$ and exact value **x** $= 4.67 \times 10^{-3}$

SIMPLIFY MATH IF POSSIBLE.
ASSUME SIMPLE APPROACH UNLESS STATED OTHERWISE or CANNOT WORK.

Pressure Equilibrium Constants

K is the general symbol for equilibrium constant
K_c is the equilibrium constant defined by concentrations
K_p is the equilibrium constant defined by partial pressures

Below shows how K_c and K_p are defined for same reaction

For reaction:

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

$K_c = [NH_3]^2 / [N_2] [H_2]^3$ K units $(mol/L)^{-2}$

$K_p = P_{NH3}^2 / P_{N2} P_{H2}^3$ K units $(atm)^{-2}$

Connection between K_c and K_p

PV= nRT → P= (n/V) RT → P= [ ] RT Note: (n/V) = [ ] concentration

So for this specific case $N_2 (g) + 3H_2 (g) \Leftrightarrow 2NH_3 (g)$

$$K_p = \frac{[NH_3]^2 (RT)^2}{[N_2] (RT) [H_2] (RT)^3} = \frac{[NH_3]^2}{[N_2] [H_2]^3} \frac{(RT)^2}{(RT)^4}$$

$Kp = Kc (RT)^{-2}$

and units in the specific case above
$(1/atm)^2 = (L/mol)^2 (mol/Latm)^2$
so remember RT units are {(L atm)/(mol K)} { K} ={ L atm/ mol } or atm/M

and in general for any reaction

$$K_p = K_c (RT)^{\Delta n} \quad \text{where} \quad \Delta n = \Sigma n_{gas}(\text{prod}) - \Sigma n_{gas}(\text{react})$$

and Δn is change in moles of gas

Example Relate K_c and K_p

Relate K_c and K_p for $CaCO_3$ (s) ⇔ CaO (s) + CO_2 (g)

Leave off pure solids then

$K_c = [CO_2]$ or $K_p = P_{CO2}$

and the connection between them is
$K_p = K_c (RT)^1$ where $\Delta n = (1) - (0) = +1$ because only gas considered

Check Units
atm = [M] {atm/M} so units check

Example - Find Partial Pressure of CO (P_{CO})

Given:
C (s) + CO_2 (g) ⇔ 2CO (g) at T = 1000°C
K_p = 167.5 atm and P_{CO2} = 0.10atm at equilibrium

(a) then write K expression

$$K_p = P_{CO}^2 / P_{CO2}$$

(b) sub in numbers

$$167.5 \text{ atm} = P_{CO}^2 / 0.10\text{atm}$$

(c) and solve

$$(167.5 \text{ atm}^2)(0.10\text{atm}) = P_{CO}^2$$

or $$(P_{CO}^2)^{1/2} = (16.75\text{atm}^2)^{1/2}$$

$$P_{co} = 4.10 \text{ atm}$$

Example - Find Equilibrium pressures for CO and CO_2

Given:
FeO (s) + CO (g) ⇔ Fe (s) + CO_2 (g)
K_p = 0.403atm at T = 1000°C
Start with excess of FeO, 1.0atm of CO, what are equil. conditions?

(a) write K expression and equilibrium

$K_p = P_{CO2}/ P_{CO}$ if K_p = 0.403atm
and initial pressure of CO is 1.00atm and no CO_2

$P_{CO} = (1.00 – x)$
P_{CO2} = x atm

Therefore

0.403 = x/ (1.00 – x)   Solve for x
0.403 - 0.403x = x
0.403 = 1.403x
x = 0.287atm

so equilibrium concentrations are:
P_{CO} = 0.713 atm (from $P_{CO} = (1.00 – x)$)
P_{CO2} = 0.287 atm

Change Chemical Equation then Change K expression and value

Consider a chemical reaction that involves A and B reactants
and product C
where equilibrium concentrations are [A] = 2.24 [B]=2.24 and [C]=50
and balanced equation is

A + B ⇔ 2C

so therefore value of K is

$$\mathbf{K = \frac{[C]^2}{[A]\,[B]}}$$

K= $(50)^2$/ (2.24) (2.24)
K= 2500/ (5.018)
K= 498

if the balanced equation is written instead as

$$(1/2)A + (1/2)B \Leftrightarrow C$$

then

$$K = \frac{[C]}{[A]^{1/2}[B]^{1/2}}$$

$$K = 50/[(2.24)^{1/2} (2.24)^{1/2}]$$

$$\mathbf{K = 22.32}$$

If you change the equilibrium by multiplying or dividing by number must also change the K expression and the value of the new K. In example above dividing reaction by 2 is same as taking square root of K note that $498 = (22.32)^2$.
K is specific for the reaction as written.

Le Chatlier's Principle –general rule

A system at equilibrium reacts to a stress to remove the stress and reestablish equilibrium. For example: Increase something on one side then after that change the equilibrium moves to other side (shifts toward other side) in a chemical reaction.

Increase amount then shifts away.
Decrease amount then shifts toward.

Le Chatlier's Principle –examples
Consider:
a) Concentration
b) Pressure
c) Temperature

(a) Concentration
If concentration of substance increased equilibrium will shift to decrease concentration (to opposite side).

Example: for equilibrium

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

if

Increase H_2 then shift toward right →
Increase HI then shift toward left ←
Decrease H_2 then shift toward left ←
Decrease HI then shift toward right →

Removal of products can drive reaction to completion even if equilibrium does not favor.
Remember shift is after the initial change.
Maybe more at start but decrease after addition.
Think of it like a balance that must be reestablished

Le Chatlier's Principle in simple terms is
Increase- shift away
Decrease- shift toward

(b) Pressure

For gases, the effect of pressure is most important and less so for solids and liquids.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
More gas on products side
pressure increase then shift left ←
pressure decrease then shift right →

to predict pressure effect find the side that has the most gas on it. If same amount of gas on both sides then will not have effect.
If pressure increased and
= more gas ← shift left
same gas = same gas no change
more gas = shift right →

Example – ice skating
Small changes in pressure do not much affect sold or liquid.
Exception, phase change if density is quite different

	H_2O (s)	⇔	H_2O (l)
Lower Density	(more Vol.)		(less Vol.)

So in ice skating the weight on small metal blade exerts large pressure and Increase P causes shift from solid to liquid so ice melts in thin layer and skater slides along on layer of water on top of ice. After pressure is removed, it refreezes.

Example – lung damage
(COPD) Chronic Obstructive Pulmonary Disease
(from for example long term smoking) damages lungs so
cannot exhale CO_2 effectively, builds up in lungs and if CO_2 increased then

$$CO_2\,(g) \;+\; H_2O(l) \Leftrightarrow \underset{\text{Carbonic acid}}{H_2CO_3\,(aq)} \Leftrightarrow H^+\,(aq) \;+\; HCO_3^-\,(aq)$$

CO_2 increased in above equilibrium so have more carbonic acid in blood and so blood becomes too acidic. This condition can cause severe illness or death.

c) Temperature

Increase temperature causes shift away from side with heat.
Lower temperature causes shift toward side with heat.

Exothermic ΔH (-)

$$A \Leftrightarrow B + \text{heat}$$

Endothermic ΔH (+)

$$\text{Heat} + A \Leftrightarrow B$$

Temp change causes change the value of the equilibrium constant not just the relative concentrations.

Example for endothermic reaction below

$\Delta H = +41.1kJ$

$$41.1kJ + CO_2 + H_2 \Leftrightarrow CO + H_2O$$

you expect that raising temperature will shift reaction to right and we observe

K(700°C) = 0.63

K (1000°C) = 1.66 equilibrium constant more toward products at higher T

Catalyst- no effect on equilibrium position or values of K
but it does causes equilibrium to be reached faster because rate greater

<u>Example of Effect of LeChatlier's Principle</u>

Given:

$A \Leftrightarrow 2B$ and $K= [B]^2/ [A]$ and $K=8$

then at equilibrium if [B] = 4 and [A] = 2 → $K=(4^2/ 2) = 8$ Correct

Now increase A from 2 to 4 and watch for shift

	Initial	Δ	Final	Final(shown below)
A	4	-x	4 - x	4 - 0.605 = 3.395
B	4	+2x	4 + 2x	4 + 2(0.605) = 5.210

$8 = (4 + 2x)^2 / (4-x)$

$32 - 8x = 16 + 16x + 4x^2$

$0 = -16 + 24x + 4x^2$ Divide by 4

$x^2 + 6x - 4 = 0$

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

$$\frac{-6 \pm \sqrt{(6^2 - 4 (1) (-4))}}{2 (1)}$$

$$\frac{-6 \pm \sqrt{(56)}}{2}$$

$x = \frac{-6 + 7.21}{2}$ $x = \frac{-6 - 7.21}{2}$

x = 0.605 or -6.61 so must be x=0.605 and then
[A] = 4 – x = 3.395 [B] = 4 + 2x = 5.210

and check results:

$K = [5.210]^2 / [3.395] = 8.00$ so correct

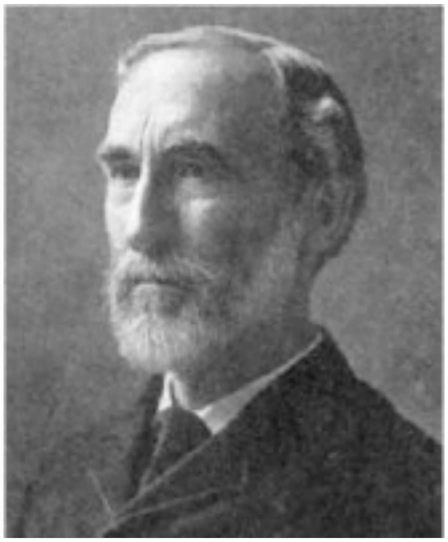
Note K value is unchanged since T not changed

Both [A] and [B]are higher than original equilibrium values but LeChatelier's question asked what happened after A added
and predicts shift to more B and less A

what we calculate is;
initially [A] = 2 and [B] = 4
then stress caused by increasing [A] to 4 and now what happens?
observe response is [A] = 4 → 3.395 and [B] = 4 → 5.210
so after stress of adding A then less A and more B

ΔG and Equilibrium

Josiah Willard Gibbs



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$\Delta G = \Delta G° + RT \ln Q$

ΔG = Free Gibbs Energy, Q "driving force"
$\Delta G°$ = ΔG at standard state
Q = Reaction quotient
(written like K, but can be any concentration mixed together)

If:

Q > K	**too many products**
Q = K	**at equilibrium**
Q < K	**need more products**

At Q = K, $\Delta G = 0$ → **$\Delta G° = -RT \ln K$**
$K = e^{-(\Delta G/RT)}$

Example
If $K = 1.00\text{x}10^9$ find value of ΔG

$\Delta G° = -(8.31\ \text{J/mol K})(298\text{K}) \ln(1.00\text{x}10^9)$
$\Delta G° = -51{,}319$ J/mol or -51.3kJ/mol
but usually drop mol and just write $\Delta G° = -51.3\text{kJ}$

Example
If Q = 1.00 x10^{-3} what is ΔG

G = ΔG° + RT lnQ
ΔG = -51,300 + (8.31J/mol K) (298K) ln (1.00x10^{-3})
ΔG = -51,300 + (-17,100) = -68,400J or -68.4 kJ

Meaning because too few products, there is an even stronger "driving force" (bigger negative ΔG) toward products.

<u>ΔG and K connection</u>

ΔG°	**K**	**meaning**
-	**>1 (large)**	**products favored**
0	**= 1**	**balance**
+	**< 1 (small)**	**reactants favored**

ΔG and Equilibrium

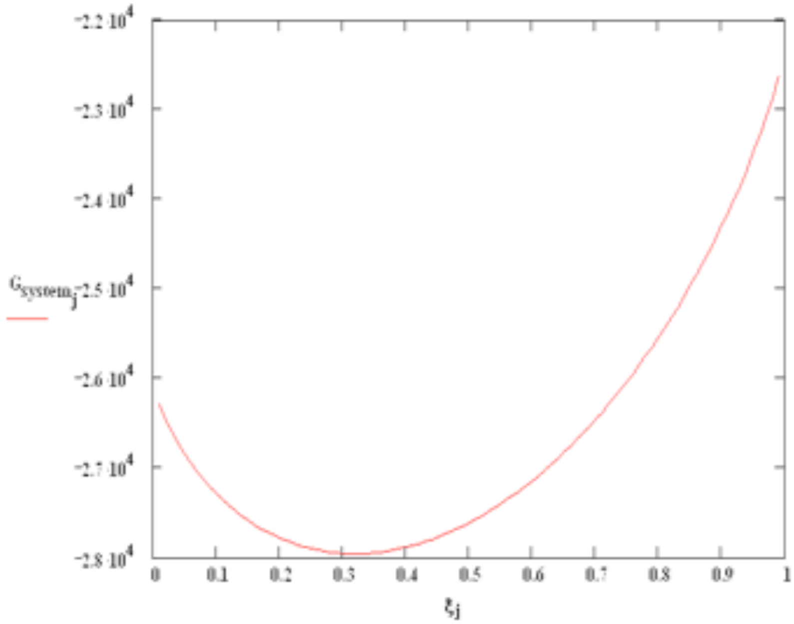
ΔG = ΔG° + RT lnQ

ΔG = Free energy as Q varied driving force
ΔG° = Free energy of gas at 1atm at standard state
Q = Reaction quotient (ratio prod/reactants) using any concentrations

ΔG = ΔG° if Q = 1

A (g) ⇔ B (g)   Equilibrium occurs at lowest free energy

<u>Go to lowest G</u>
On graph below system will go to lowest value of G plotted along y axis so ΔG change will always be negative.



http://jchemed.chem.wisc.edu/JCEDLib/SymMath/collection/032/sm032fig1.gif

Miscellaneous Practice

a) What is K?

Equilibrium Constant, K = Products/ Reactants, tells us relative amounts of products and reactants using gas concentration in solution (not pure liquid or solid concentrations).

b) Write K_p expression for reaction below
A + 2B ⇔ 3C

$K = P_C^3 / (P_A \; P_B^2)$

c) Given expression below solve for K
$\Delta G° = -RT \ln K$

$K = e^{-(\Delta G/RT)}$

d) At equilibrium what is Q equal to and what is ΔG equal to

since $\Delta G = \Delta G° - RT \ln Q$
Q = K at equilibrium
and $\Delta G = - RT \ln (K) + RT \ln (K)$

so $\Delta G = 0$

meaning since at equilibrium no driving force ΔG to get there

e) If ΔG= - 51.319kJ/mol what is K

$$K = e^{-(-51319J/mol)/(-8.31J/mol\ K)*298K)} = 1.00x10^9$$

f) What is the effect of positive ΔH and ΔS on ΔG and if reaction will occur

ΔH	favor reaction occur	ΔS	favor reaction occur
-	yes	-	no
+	no	+	yes

ΔH	ΔS	ΔG = ΔH –TΔS	
-	+	-	will occur
+	-	+	not occur
-	-	?	at low T will occur
+	+	?	at high T will occur

In other words since ΔG = ΔH –TΔS and T is always positive then

Reactions favored if system gives off heat ΔH= (-)
or system increases entropyΔS = (+)

and Enthalpy dominates at low Temp.
Entropy dominates at high Temp.

At room Temp generally exothermic reactions ΔH = (-) will go

g) make reaction table (ICE) for chemical equation A ⇔ 2B
if [A] = 1.00 initially

	Initial	**C**hange	**E**quilibrium
A	1.00	-x	1.00-x
B	0	+2x	2x

h) make reaction table for chemical equation 3A ⇔ B
if [A] = 0.50

	Initial	Change	Equilibirum (final)
A	0.50	-3x	0.50-3x
B	0	+x	x

Industrial Example - Ammonia Synthesis

N_2 (g) + $3H_2$ ⇔ $2NH_3$ (g) + heat

for reaction above equilbirum constants are shown below

T	K
398K	57
298K	812
198K	1.6×10^5

Equilibrium favors products at high pressure and low temperature.

However, speed of reaction favored at high temperature.

Industrial synthesis is done at high pressure (favors products)
and high temperature even though does not favor products it is more important to make reaction go faster

Ammonia synthesis carried out in industry at P= 400atm and T= 773K or 500°C

Catalyst is essential to get reaction to occur and catalyst is mixture of

Catalyst		Promoters
Fe	Fe_2O_3	Al_2O_3 K_2O

Steps are
a) gases adsorb on iron catalyst surface
b) new N-H bonds are formed
c) product ammonia NH_3 desorbs from surface
d) ammonia removed and unreacted N_2 and H_2 gases are recycled to react again