

Last Time

TABLE 6.1 Results of Three Experiments for the Reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
I	$[\text{N}_2]_0 = 1.000 \text{ M}$ $[\text{H}_2]_0 = 1.000 \text{ M}$ $[\text{NH}_3]_0 = 0$	$[\text{N}_2] = 0.921 \text{ M}$ $[\text{H}_2] = 0.763 \text{ M}$ $[\text{NH}_3] = 0.157 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$
II	$[\text{N}_2]_0 = 0$ $[\text{H}_2]_0 = 0$ $[\text{NH}_3]_0 = 1.000 \text{ M}$	$[\text{N}_2] = 0.399 \text{ M}$ $[\text{H}_2] = 1.197 \text{ M}$ $[\text{NH}_3] = 0.203 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$
III	$[\text{N}_2]_0 = 2.00 \text{ M}$ $[\text{H}_2]_0 = 1.00 \text{ M}$ $[\text{NH}_3]_0 = 3.00 \text{ M}$	$[\text{N}_2] = 2.59 \text{ M}$ $[\text{H}_2] = 2.77 \text{ M}$ $[\text{NH}_3] = 1.82 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$

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Each equilibrium has different concentrations, but the same value for Kc

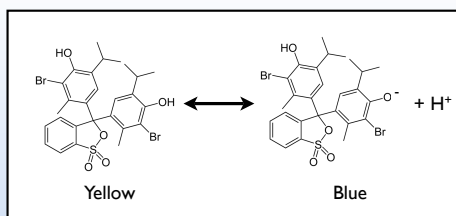
Equilibria and Perturbations (Stress)

What happens to a system at equilibrium if I change something like

The concentration of one of the chemicals

The Pressure

The Temperature



In my demo last time, when the solution was a deep blue and at equilibrium. I then perturb the system by adding a strong acid which had a high concentration of H^+ . What did the reaction mixture do?

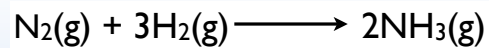
- A. the reaction shifted to a new equilibrium high in "reactant" concentration
- B. the reaction was unchanged as it was already at equilibrium
- C. the reaction generated even more "products"

Qualitatively Understanding "stress"

Le Chatelier's Principle

If a chemical system at equilibrium experiences a change,

then the equilibrium shifts to partially counter-act the imposed change.



You find the system at equilibrium,
then you decide to add more H_2 to the mixture

What happens as the reaction goes to a new equilibrium?

A. the concentration of N_2 decreases

The system will compensate by moving
to "reduce" the stress.

You added H_2

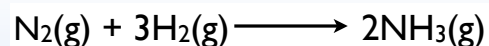
The reaction will try to reduce the amount of H_2

Stressing the concentrations

Add Reactants \longrightarrow Reaction Shifts
towards Product

Add Products \longrightarrow Reaction Shifts
towards Reactants

What if I increase the pressure?



You find the system at equilibrium at 1 atm,
then you decide to increase the pressure to 2 atm.

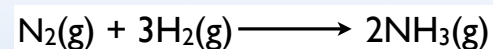
What happens as the reaction goes to a new equilibrium?

A. moves towards the products as they have fewer molecules

You increased the pressure

The reaction will try to reduce the pressure
the only way to do this is to reduce the number of
molecules (move toward products)

Dealing with Stress from a Quantitative Perspective



Equilibrium

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

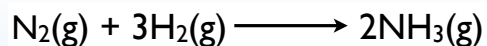
$$[\text{N}_2] = 0.921 \text{ M}$$

$$[\text{H}_2] = 0.763 \text{ M}$$

$$[\text{NH}_3] = 0.157 \text{ M}$$

$$K_c = \frac{[0.157]^2}{[.921][.763]^3} = 0.06$$

If I increase $[\text{N}_2]$ to 3 M the system will no longer be at equilibrium.
Which way will it shift to get back to equilibrium?



Not at equilibrium

$$\begin{aligned} [\text{N}_2] &= 3 \text{ M} \\ [\text{H}_2] &= 0.763 \text{ M} \\ [\text{NH}_3] &= 0.157 \text{ M} \end{aligned}$$

not at equilibrium

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$Q = \frac{[0.157]^2}{[3][.763]^3} = 0.0185$$

$$Q = 0.0185$$

$$K = 0.06$$

$$Q < K$$

therefore reaction needs to
increase products to get to equilibrium

K is constant

$$K = \frac{\text{Products}}{\text{Reactants}}$$

Constant!

So if products goes up
the reaction will shift to get
back to the same constant ratio

This can happen if
Product goes down slightly
and Reactant goes up slightly

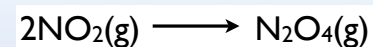
Increasing Pressure



$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{X_{\text{N}_2\text{O}_4} P}{X_{\text{NO}_2}^2 P^2} = \frac{X_{\text{N}_2\text{O}_4}}{X_{\text{NO}_2}^2 P}$$

If you increase P
Then the mole fraction of NO₂
must go down since K is constant

Relating K_p and K_c

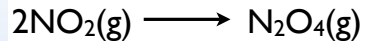


$$K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \quad K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

$$P_{\text{N}_2\text{O}_4} = \frac{n_{\text{N}_2\text{O}_4} RT}{V} = [\text{N}_2\text{O}_4] RT$$

concentration

Relating K_p and K_c



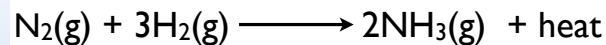
$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{[\text{N}_2\text{O}_4]RT}{[\text{NO}_2]^2(RT)^2} = K_c \frac{1}{RT}$$

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

In general $K_p = K_c(RT)^{\Delta n}$

Δn is the change in the number of moles of gas

Temperature Change



this reaction is exothermic

If you increase T then to "partially compensate" the reactions shifts to the reactants (consuming heat)

How to change the pressure (constant T)

Increase P (decrease V) Shifts to side with fewer gas molecules

Decrease P (increase V) Shifts to side with more gas molecules

Add an inert gas (one that doesn't react. Like He)

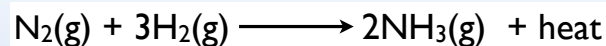
Constant P

This is like diluting the system
increase in V
like lowering P
shift to side with more gas molecules

Constant V

This is like essentially doing nothing
The partial pressures of all the
molecules that matter are unchanged
(the number of collisions is
unchanged)
the reaction is unchanged

Why does Temperature Change Equilibrium?



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

K is a function of T!

$$\Delta_R G^\circ(T) = -RT \ln K$$

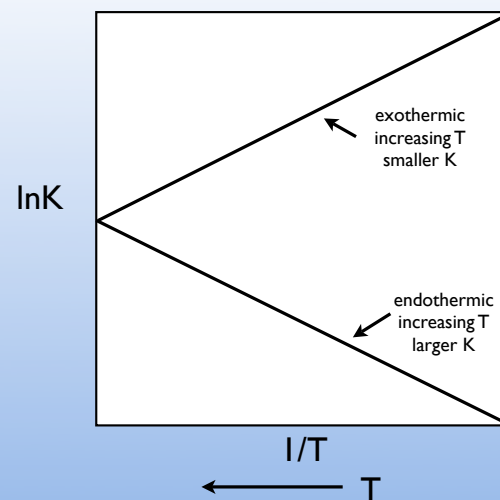
$$\Delta_R G^\circ(T) = \Delta_R H^\circ - T \Delta_R S^\circ$$

$$-RT \ln K = \Delta_R G^\circ(T) = \Delta_R H^\circ - T \Delta_R S^\circ$$

$$\ln K = -\Delta_R H^\circ / RT + \Delta_R S^\circ / R$$

Temperature dependence of K depends on $\Delta_R H^\circ$

$$\ln K = -\Delta_R H^\circ / RT + \Delta_R S^\circ / R$$



$y = mx + b$
y is $\ln K$
x is $1/T$
m is $-\Delta_R H^\circ / R$
b is $\Delta_R S^\circ / R$

a different way to do
calorimetry
measure K to find
 $\Delta_R H^\circ$

Some Calculations