Last Time

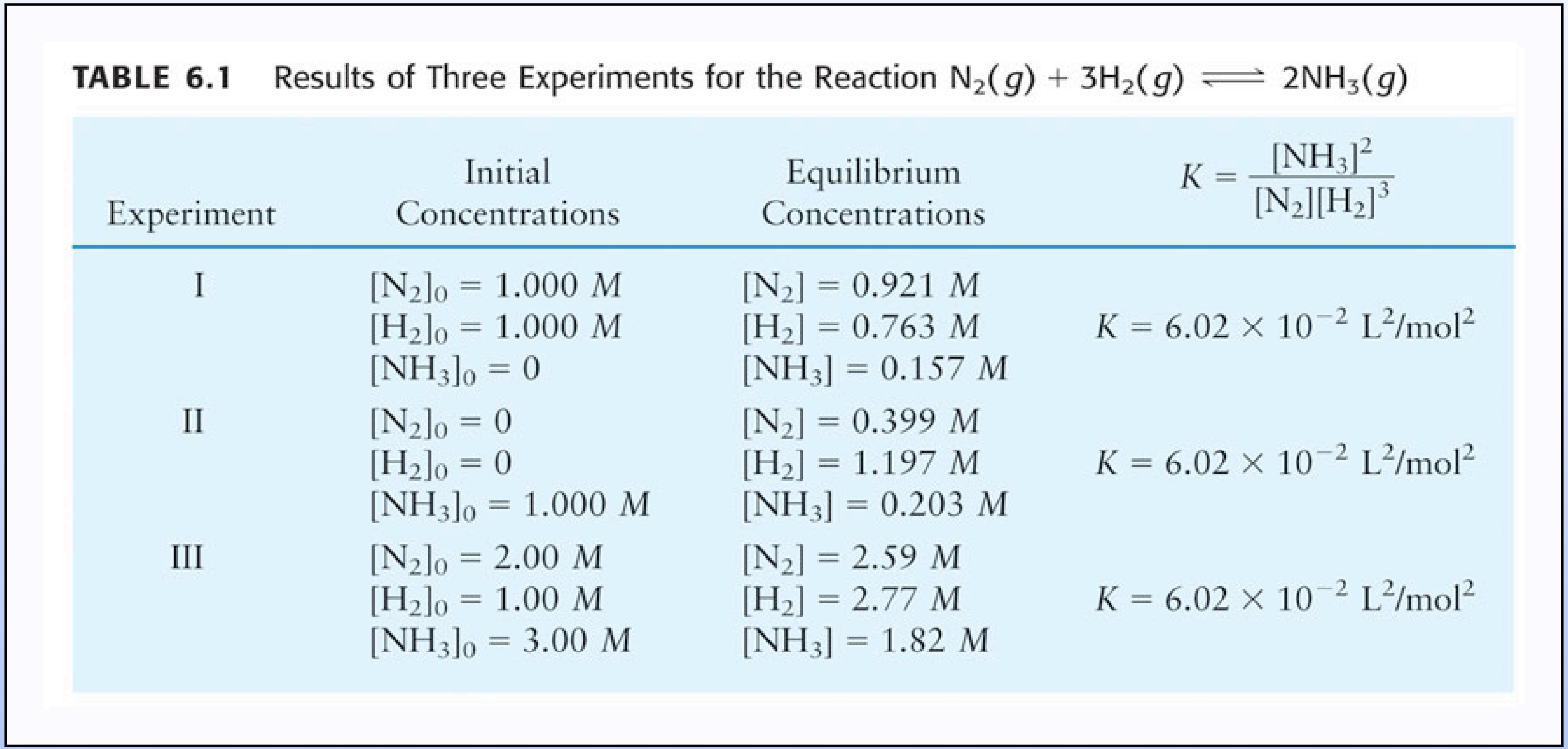


TABLE 6.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$

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

Relating $\Delta_R G°$ to K

$$\Delta_R G° = -RT\ln K$$

$$K = \exp(-\Delta_R G°/RT)$$

$\Delta_R G° < 0$ then $K > 1$ favors products

$\Delta_R G° > 0$ then $K < 1$ favors reactants

K can be very large or very small

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

for the following reaction $\Delta_R G° = -474\ \text{kJ mol}^{-1}$
at 300K the equilibrium constant is

A. $K = 1$

B. $K = 0.25$

C. $K = 1.55 \times 10^{-83}$

D. $K = 6.83 \times 10^{82}$

this is the only one >1
-474 kJ mol^{-1} is "big"

$$K = e^{+190}$$

$$2HgO(s) \longrightarrow O_2(g) + 2Hg(l)$$

for the following reaction $\Delta_R G° = +194$ kJ mol^{-1}
at 300K the equilibrium constant is

A. $K = 1$

B. $K = 85{,}432$

C. $K = 1.66 \times 10^{-34}$

D. $K = 7.23 \times 10^{33}$

this is the only one <1
194 kJ mol^{-1} is “big”

$K = e^{-78}$

$$CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H^+(aq)$$

for the following reaction at 300K $K = 1.78 \times 10^{-5}$

$\Delta_R G°$ for this reaction is

A. $\Delta_R G° = 0$

B. $\Delta_R G° = -10.4\ \text{kJ mol}^{-1}$

C. $\Delta_R G° = -312\ \text{kJ mol}^{-1}$

D. $\Delta_R G° = +3.28\ \text{kJ mol}^{-1}$

this is the only one >0
equilibrium constant not
hugely small or hugely large

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

Qualitatively Understanding "stress"

Le Chatlier's Principle

If a chemical system at equilibrium experiences a change,

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

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

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 ⟶ Reaction Shifts towards Product

Add Products ⟶ Reaction Shifts towards Reactants

What if I increase the pressure?

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

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 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

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

Equilibrium

$[N_2] = 0.921$ M
$[H_2] = 0.763$ M
$[NH_3] = 0.157$ M

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

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

If I increase $[N_2]$ to 3 M the system will no longer be at equilibrium.
Which way will it shift to get back to equilibrium?

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

not at equilibrium

Not at equilibrium

$[N_2] = 3$ M
$[H_2] = 0.763$ M
$[NH_3] = 0.157$ M

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

$$Q = \frac{[0.157]^2}{[3][.763]^3} = .0185$$

$Q = 0.0185$
$K = 0.06$
$Q < K$
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

Two equilibrium constants

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

Concentrations

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

solutions

Partial Pressures

$$K_p = \frac{P_{NH3}^2}{P_{N2}P_{H2}^3}$$

gas

Increasing Pressure

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

$$K_p = \frac{P_{N2O4}}{P_{NO2}^2} = \frac{X_{N2O4}\ P}{X_{NO2}^2\ P^2} = \frac{X_{N2O4}}{X_{NO2}^2\ P}$$

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

Relating K_p and K_c

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

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} \qquad K_p = \frac{P_{N2O4}}{P_{NO2}{}^2}$$

$$P_{N2O4} = \frac{n_{N204}RT}{V} = [N_2O_4]RT$$

concentration

Relating K_p and K_c

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

$$K_p = \frac{P_{N2O4}}{P_{NO2}{}^2} = \frac{[N_2O_4]RT}{[NO_2]^2(RT)^2} = K_c\frac{1}{RT}$$

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

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

Δn is the change in the number of moles of gas

Temperature Change

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + \text{heat}$$

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?

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + \text{heat}$$

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

K is a function of T!

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

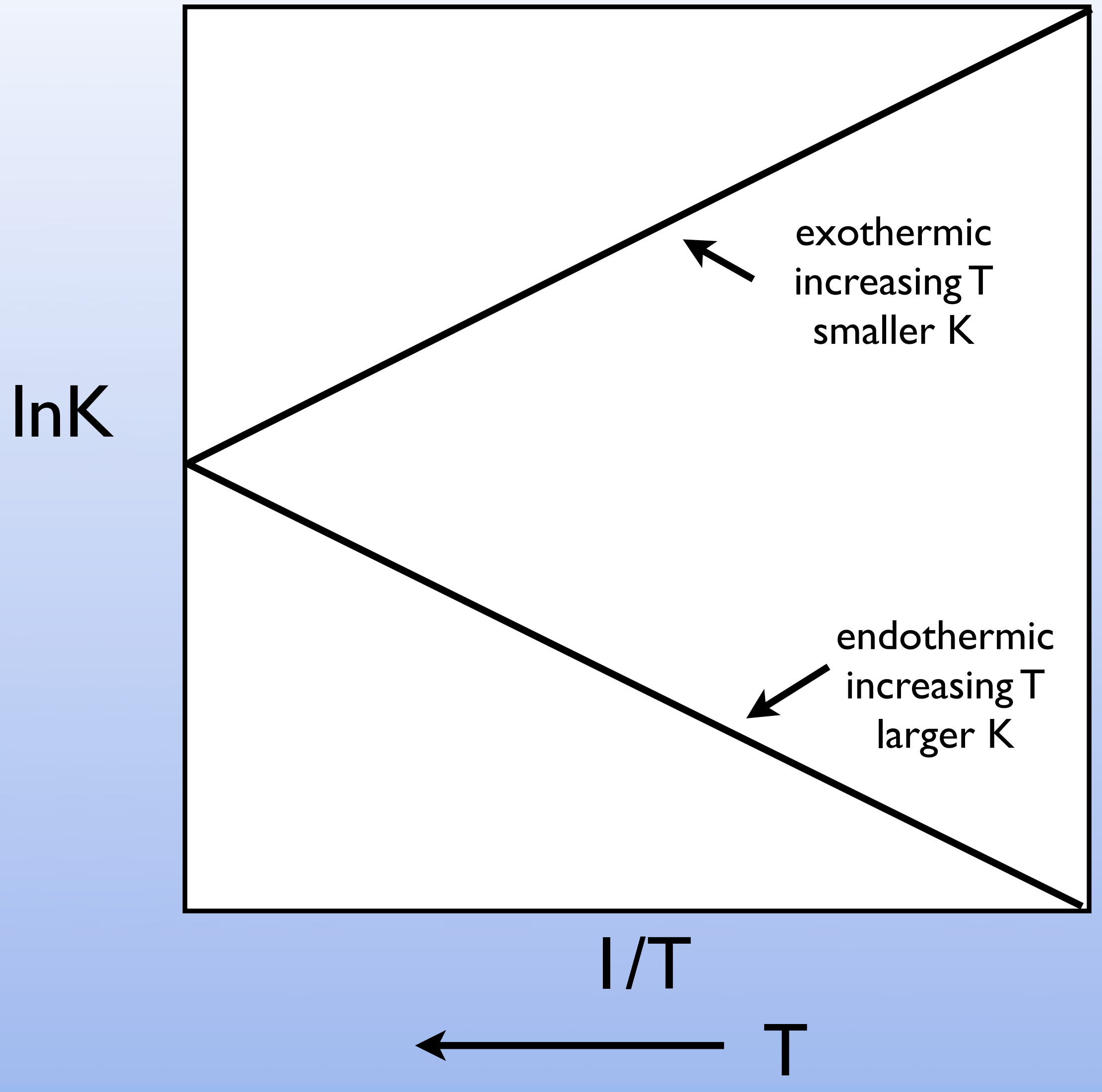
$$\Delta_R G^\circ(T) = \Delta_R H^\circ - T\,\Delta_R S^\circ$$

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

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

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

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



$y = mx + b$

y is $\ln K$

x is $1/T$

m is $-\Delta_R H°/R$

b is $\Delta_R S°/R$

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

Drug Binding Question

Ezyme/Drug Complex ⟶ Drug + Enzyme

inhibited functioning

The equilibrium for this constant is 10^{-6} (I made this up)
at what concentration of drug is half the enzyme inhibited?
(note: at this point [enzyme]=[complex])

A. $K = 1$

B. $K = 10^{2}\ \mathrm{M}$

C. $K = 10^{-3}\ \mathrm{M}$

D. $K = 10^{-6}\ \mathrm{M}$

$$K = \frac{[\text{drug}][\text{enzyme}]}{[\text{complex}]}$$

$$[\text{drug}] = K\,\frac{[\text{complex}]}{[\text{enzyme}]}$$

$$[\text{drug}] = K$$