

EQUILIBRIUM

Additional, Supplemental Text: "Solving Equilibrium Problems with Applications to Qualitative Analysis," S. Zumdahl

Refresher on equilibrium:

dynamic equal amt reactant \leftrightarrow equal amt product
 equal rates not equal amounts > one side "favored"

concentrations of R + P remain constant
 seems unchanging
 (same formed as consumed)

Why does equilibrium occur?

* rxns are reversible

- depends on energy of reactants vs. products
- depends on entropy



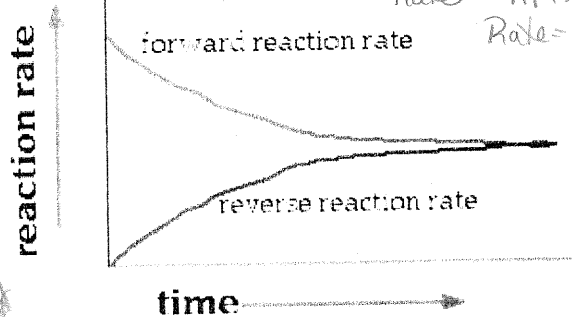
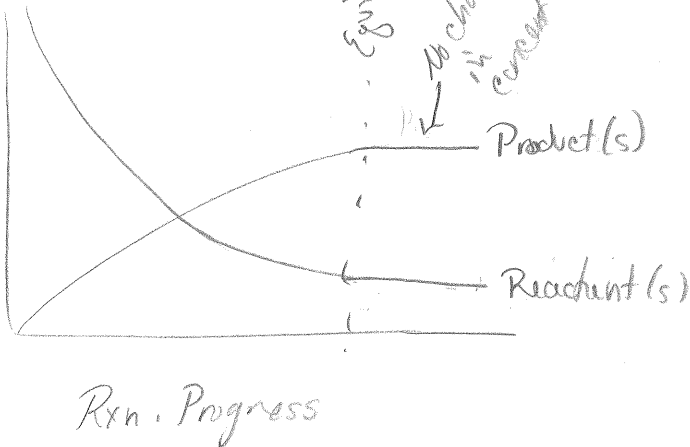
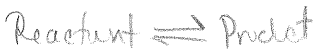
as concentration increases, more collisions allow reverse rxn

$$\text{Rate} = k_f [A]^x [B]^y$$

$$\text{Rate} = k_r [C]^m [D]^n$$

k are not equal
 But rates are

* minimum energy ~
 + max disorder



need closed vessel for eq.

What might we want to know about a system in equilibrium?

- more R or P?
- conc. of reactant or p?
- how respond to stress.
- how long to reach eq?

The Equilibrium Expression & The Equilibrium Constant (K)

1.2



Equilibrium Position is Constant / consistent

Law of Mass Action

relationship of conc + coefficients established through eqpt. equilibrium constant (per a certain temp.)

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

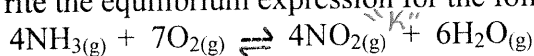
concent products / concent reactants

each raised to power = coefficient of balanced equation

entire thing called "equilibrium expression"

What info can K reveal?
ratio of react to products?

Ex: Write the equilibrium expression for the following reaction:



$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$

Solids + liquids not included in concentration expressions
do not affect K

K has no units (complex reason)

"homogeneous" vs. "heterogeneous" equilibria

K reveals the "equilibrium position"

eg. constant ≠ eq. position

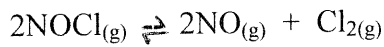
There is only 1 K for a rxn at a certain Temp ~ but an infinite # of equil. concentrations

K determined by Temp & Rxn.

Infinite eq. positions (ratios of [] that yield K) depends on initial concentrations

see demo of an rxn 6/7 of text (Ex 13.3)

Ex: Consider the reaction



at 35°C, when 3.00 mol NOCl, 1.00 mol NO, and 2.00 mol Cl₂ are mixed in a 10.0 L flask. After the system has reached equilibrium the concentrations are observed to be

$$[\text{Cl}_2] = 1.52 \times 10^{-1} \text{ M}$$

$$[\text{NO}] = 4.00 \times 10^{-3} \text{ M}$$

$$[\text{NOCl}] = 3.96 \times 10^{-1} \text{ M}$$

Calculate the value of K for this system at 35°C.

$$K = \frac{[\text{NO}]^2 [\text{Cl}_2]}{[\text{NOCl}]^2}$$

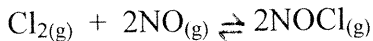
$$= \frac{(4.00 \times 10^{-3} \text{ M NO})^2 (1.52 \times 10^{-1} \text{ M Cl}_2)}{(3.96 \times 10^{-1} \text{ M NOCl})^2} = 1.55 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$= \frac{(4.00 \times 10^{-3} \text{ M NO})^2 (1.52 \times 10^{-1} \text{ M Cl}_2)}{(3.96 \times 10^{-1} \text{ M NOCl})^2} = 1.55 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

or simply

$$1.55 \times 10^{-5}$$

Ex: Calculate the value of K for the reaction:

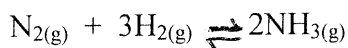


$$K = \frac{[\text{NOCl}]^2}{[\text{Cl}_2] [\text{NO}]^2} = \frac{(3.96 \times 10^{-1} \text{ M NOCl})^2}{(1.52 \times 10^{-1} \text{ M}) (4.00 \times 10^{-3} \text{ M})^2} = 6.45 \times 10^4 \frac{\text{L}}{\text{mol}}$$

$$K_{\text{reverse}} = \frac{1}{K_{\text{forward}}}$$

$$= \frac{1}{1.55 \times 10^{-5} \frac{\text{mol}}{\text{L}}} = 6.45 \times 10^4 \frac{\text{L}}{\text{mol}}$$

Ex: The following equilibrium concentrations were observed for the Haber process at 127°C:

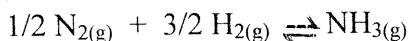


$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

- Calculate the value of K at 127°C for this reaction.
- Calculate the value of the equilibrium constant at 127°C for the reaction:
 $2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g)$
- Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation



$$a) K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L}})^2}{(8.5 \times 10^{-1} \frac{\text{mol}}{\text{L}})(3.1 \times 10^{-3} \frac{\text{mol}}{\text{L}})^3} = 3.79 \times 10^4 \frac{\text{L}^2}{\text{mol}^2}$$

$$b) K_{\text{rev}} = \frac{1}{K_{\text{forw}}} = \frac{1}{3.79 \times 10^4 \frac{\text{L}^2}{\text{mol}^2}} = 2.64 \times 10^{-5} \frac{\text{mol}^2}{\text{L}^2}$$

$$c) K_{\text{new}} = \frac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}$$

$$\text{factor} = n = \frac{1}{2} \therefore K_{\text{new}} = K^{1/2} = (3.79 \times 10^4 \frac{\text{L}^2}{\text{mol}^2})^{1/2} = 1.95 \times 10^2 \frac{\text{L}}{\text{mol}}$$

$$K_{\text{new}} = \frac{(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L}})}{(8.5 \times 10^{-1} \frac{\text{mol}}{\text{L}})^{\frac{1}{2}} (3.1 \times 10^{-3} \frac{\text{mol}}{\text{L}})^{\frac{3}{2}}} = 1.95 \times 10^2 \frac{\text{L}}{\text{mol}}$$

When balanced equation is multiplied by factor "n",
K is raised to the nth power.

$$K_{\text{new}} = (K_{\text{original}})^n$$

*K values are usually written without units.

*When the balanced equation is multiplied by a factor n , the K for the new reaction (K_{new}) is raised to the n th power:

$$K_{\text{new}} = (K_{\text{original}})^n$$

*The equilibrium expression is the reciprocal of that for a reaction written in reverse.

K in terms of PRESSURES

Equilibria involving gases can be described/expressed in terms of pressures or concentrations.

Relationship of pressure and concentration of a gas:

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT$$

Concentration = C

$$P = CRT$$

$$C = \frac{P}{RT}$$

For the ammonia synthesis reaction:

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

here first

In terms of partial pressures of the gases:

$$K_p = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

K & K_p related

③ Example on next page

⑤

$$K_c = \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} \rightarrow \frac{\left(\frac{P_{\text{NH}_3}^2}{(RT)^2}\right)}{\left(P_{\text{N}_2}\right)\left(P_{\text{H}_2}\right)^3 \cdot (RT)^2}$$

Relationship of K_c & K_p =

$$= \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \cdot (RT)^2$$

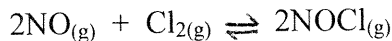
$$\therefore K = K_p \cdot (RT)^2$$

$$K = K_p (RT)^{\Delta n}$$

coefficients R-P
 $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$
 $4 - 2$

First
 $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Ex: The reaction for the formation of nitrosyl chloride:



was studied at 25°C. The partial pressures were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

Calculate the value of K_p for this reaction at 25°C.

$$K_p = \frac{(P_{\text{NOCl}})^2}{(P_{\text{NO}})^2 (P_{\text{Cl}_2})}$$

$$= \frac{(1.2 \text{ atm})^2}{(5.0 \times 10^{-2} \text{ atm})^2 (3.0 \times 10^{-1} \text{ atm})} = \underline{1.92 \times 10^3 \text{ atm}^{-1}}$$

K?

$$K = K_p (RT)^{\Delta n} = 1.92 \times 10^3 \text{ atm}^{-1} \left[\frac{(0.08206 \text{ L} \cdot \text{atm})}{\text{K} \cdot \text{mol}} (298 \text{ K}) \right]^{3-2}$$

$$= 4.70 \times 10^4 \frac{\text{L}}{\text{mol}}$$

Relationship of K and K_p :

$K \neq K_p$
usually

only when coeff of reactants = coefficients of products (then RT cancel)

$$K_p = K (RT)^{\Delta n} \quad K = K_p (RT)^{\Delta n}$$

$\Delta n = \text{coeff. product} - \text{coeff. reactant}$

Ex: Using the value of K_p from the previous problem, calculate the value of K at 25°C for the reaction: $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2\text{NOCl}_{(g)}$

$$K = K_p (RT)^{\Delta n}$$

$$= (1.92 \times 10^3 \text{ atm}^{-1}) \left(\frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (298 \text{ K})$$

$$= 4.70 \times 10^4 \frac{\text{L}}{\text{mol}}$$