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[TP] At 25°C, the equilibrium constant of $2 A(g) \rightleftharpoons 3 B(g)$ 1.5×10^{11} . Amounts 4.0 atm A and 2.0 atm B are combined in sealed, rigid container. The amount of A at equilibrium will be ...

0% 1. $\ll 2$ atm
 0% 2. ≈ 2 atm
 0% 3. ≈ 4 atm
 0% 4. ≈ 8 atm
 0% 5. $\gg 8$ atm
 0% 6. Some other amount
 100% 7. Not sure

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Lecture 14 CH131 Summer 1 2021
 Tuesday, June 22, 2021

- Approximating equilibration
- Equilibrium calculation examples
- Disturbing equilibrium
- Effect of temperature on equilibrium: $\Delta G = RT \ln(Q/K) = \Delta H - T\Delta S$

Next: Chapter 16: Solubility equilibria; Begin ch15: Acid-base equilibria

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Approximating equilibration

When the equilibrium constant is either very big or very small, the calculation of equilibrium amounts is greatly simplified.

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Approximating equilibration

When $K \ll 1$, the equilibrium amounts will be mostly reactants. This means a good starting point is to adjust the initial amounts so that the amount of limiting product is 0.

The reason this is a good starting point is that the small amount of product that must form to achieve equilibrium will change the amount of reactants negligibly.

$$A \rightarrow B$$

$$I \quad z \quad 3$$

$$E \quad \quad \approx 0$$

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6} //$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3	2	1
Revised Initial			
Change			
Equilibrium			≈ 0

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6}$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3 +1	2 -1	1 -1
Revised Initial	4	1	0 //
Change	-X	+X	+X
Equilibrium			

$10^6 \times \frac{1A}{1B \cdot 1C} = 1A$
 $10^6 \times \frac{1B}{1C} = 1B$

$B + C \rightarrow A \quad 100\%$
 I 2 1 3
 C -1 -1 +1
 F 1 0 4

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6}$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3	2	1
Revised Initial	4	1	0
Change	-x	+x	+x
Equilibrium			

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6}$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3	2	1
Revised Initial	4	1	0
Change	-x	+x	+x
Equilibrium	$4 - x \approx 4$	$1 + x \approx 1$	x

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6}$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3	2	1
Revised Initial	4	1	0
Change	-x	+x	+x
Equilibrium	$4 - x \approx 4$	$1 + x \approx 1$	x

$$K = \frac{1 \times x}{4} = 1 \times 10^{-6}$$

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Approximating equilibration

$A(g) \rightleftharpoons B(g) + C(g) \quad K = 1 \times 10^{-6}$

$$K = \frac{(1+x)x}{(4-x)}$$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3	2	1
Revised Initial	4	1	0
Change	-x	+x	+x
Equilibrium	$4 - x \approx 4$	$1 + x \approx 1$	x

$$K = \frac{1 \times x}{4} \rightarrow x = \frac{4 \times 1 \times 10^{-6}}{1} = 4 \times 10^{-6}$$

$$4 - x \approx 4$$

$$\frac{4.7777777}{4} - \frac{0.000004}{4}$$

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Approximating equilibration

When $K \gg 1$, the equilibrium amounts will be **mostly products**. This means a good starting point is to adjust the initial amounts so that **the amount of limiting reactant is 0**.

The reason this is a good starting point is that the **small amount of reactant** that must be present to achieve equilibrium **will change the amount of products negligibly**.

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[TP] At 25°C, the equilibrium constant of $2 A(g) \rightleftharpoons 3 B(g)$ (1.5×10^{11}) amounts 4.0 atm A and 2.0 atm B are combined in sealed, rigid container. The amount of A at equilibrium will be ...

0% 1. $\ll 2$ atm
 0% 2. ≈ 2 atm
 0% 3. ≈ 4 atm
 100% 4. ≈ 8 atm
 0% 5. $\gg 8$ atm
 0% 6. Some other amount
 0% 7. Not sure

	2A	3B
I	4.0	2.0
R	0	8.0
C	+2x	-3x
E	2x	8.0 - 3x

$$1.5 \times 10^{11} = \frac{(8.0 - 3x)^3}{(2x)^2} \approx \frac{(8.0)^3}{(2x)^2}$$

$$8.0 - 3x \approx 8.0$$

$$x = 0.000029$$

$$3x = 0.000087$$

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Approximating equilibration

$$2 A(g) \rightleftharpoons 3 B(g) K = 1.5 \times 10^{11}$$

	A(g)/atm	B(g)/atm
Initial	4.0	2.0
Revised Initial		
Change		
Equilibrium	≈ 0	

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Approximating equilibration

$$2 A(g) \rightleftharpoons 3 B(g) K = 1.5 \times 10^{11}$$

	A(g)/atm	B(g)/atm
Initial	4.0	2.0
Revised Initial	0	8.0
Change		
Equilibrium		

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Approximating equilibration

$$2 A(g) \rightleftharpoons 3 B(g) K = 1.5 \times 10^{11}$$

	A(g)/atm	B(g)/atm
Initial	4.0	2.0
Revised Initial	0	8.0
Change	+2x	-3x
Equilibrium		

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Approximating equilibration

$$2 A(g) \rightleftharpoons 3 B(g) K = 1.5 \times 10^{11}$$

	A(g)/atm	B(g)/atm
Initial	4.0	2.0
Revised Initial	0	8.0
Change	+2x	-3x
Equilibrium	2x //	8.0 - 3x \approx 8.0 //

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Approximating equilibration

$$2 A(g) \rightleftharpoons 3 B(g) \quad K = 1.5 \times 10^{11}$$

	A(g)/atm	B(g)/atm
Initial	4.0	2.0
Revised Initial	0	8.0
Change	+2x	-3x
Equilibrium	2x	8.0 - 3x ≈ 8.0

$$K \approx \frac{8.0^3}{(2x)^2} \rightarrow x = \sqrt{\frac{8.0^3}{4 \times 1.5 \times 10^{11}}} = 0.000029$$

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Practice: Problem 14.25

	SO ₂ Cl ₂	SO ₂	Cl ₂
I	0.720	0	0
C	-x	+x	+x
E	0.720-x	x	x

$P_{SO_2Cl_2} + P_{SO_2} + P_{Cl_2} = 6.720 - x + x + x = 1.30 \text{ atm}$
 $1.30 = 0.720 + x$
 $x = 1.30 - 0.720 = 0.58$
 $K = \frac{x^2}{0.720 - x} = \frac{0.58^2}{0.720 - 0.58} = 0.14$

25. Sulfuryl chloride (SO₂Cl₂) is a colorless liquid that boils at 69°C. Above this temperature, the vapors dissociate into sulfur dioxide and chlorine:

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

This reaction is slow at 100°C, but it is accelerated by the presence of some FeCl₃ (which does not affect the final position of the equilibrium). In an experiment, 3.174 g of SO₂Cl₂(l) and a small amount of solid FeCl₃ are put into an evacuated 1.000-L flask, which is then sealed and heated to 100°C. The total pressure in the flask at that temperature is found to be 1.30 atm.

(a) Calculate the partial pressure of each of the three gases present.
 (b) Calculate the equilibrium constant at this temperature.

$3.174 \text{ g} \times \frac{1 \text{ mol}}{M_{SO_2Cl_2}} = n_{SO_2Cl_2}$

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Practice: Problem 14.33

	N ₂	O ₂	2NO
I	0.41	0.59	0.22
E	0.52-x	0.70-x	2x

$K = 4.2 \times 10^{-31}$
 $4.2 \times 10^{-31} = \frac{(2x)^2}{(0.52-x)(0.70-x)}$

33. At 25°C, the equilibrium constant for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2 NO(g)$$

Suppose a container is filled with nitrogen (initial partial pressure of 0.41 atm), oxygen (at an initial partial pressure of 0.59 atm), and nitrogen oxide (at an initial partial pressure of 0.22 atm). Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.

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Practice: Problem 14.41

	NH ₃ (g)	HCl(g)	NH ₄ Cl(s)
I	0.80	0	some
C	+x	+x	-x
E	0.80+x	x	some

$K = \frac{1}{P_{NH_3} P_{HCl}} = 4.0 = \frac{1}{(0.80+x)x}$
 $x = 0.24$
 $P_{NH_3} = 0.80 + x = 1.04$
 $P_{HCl} = 0.24$
 $K = 4.0 = \frac{1}{(1.04)(0.24)} \rightarrow x = 0.15$

41. The equilibrium constant for the reaction

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$

at 340°C (K = 4.0)

(a) If the partial pressure of ammonia is P_{NH₃} = 0.80 atm and solid ammonium chloride is present, what is the equilibrium partial pressure of hydrogen chloride at 340°C?
 (b) An excess of solid NH₄Cl is added to a container which with ammonia at 340°C and a pressure of 1.50 atm. Calculate the pressures of NH₃(g) and HCl(g) reached at equilibrium.

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Disturbing equilibrium

Essential idea: A system at equilibrium responds to a disturbance by **partially offsetting** the disturbance.

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Practice: Problem 14.52

$\Delta G > 0$ ☹️

	SO_2Cl_2	SO_2	Cl_2
I	1.20	0	0
C	-x	+x	+x
E	1.20-x	x	x

$K = 2.4 = \frac{x^2}{1.20-x} \Rightarrow x = 0.88$

E	0.32	0.88	0.88
NI	0.64	1.76	1.76
C	+y	-y	-y
E	0.64+y	1.76-y	1.76-y

52. At $T = 100^\circ\text{C}$ the reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ has an equilibrium constant $K = 2.4$.

(a) Suppose the initial partial pressure of SO_2Cl_2 is 1.20 atm, and $P_{\text{SO}_2} = P_{\text{Cl}_2} = 0$. Calculate the reaction quotient Q and state whether the reaction proceeds to the right or to the left as equilibrium is approached.

(b) Calculate the partial pressures at equilibrium.

(c) If the volume of the system is then decreased, will there be net formation or net dissociation of SO_2Cl_2 ?

$Q = \frac{(1.76)^2}{0.64} = 4.84 > K = 2.4$

$K = 2.4 = \frac{(1.76-y)^2}{0.64+y}$

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Q versus K is the key to spontaneity

If $Q < K$, product must form to get to equilibrium, so **spontaneous**

If $Q > K$, reactants must form to get to equilibrium, so **nonspontaneous**

This means ΔG is proportional to $\ln(Q/K)$.

The constant of proportionality turns out to be RT .

$\Delta G = RT \ln(Q/K) = \Delta H - T\Delta S$

$Q < K, \Delta G < 0, \frac{Q}{K} < 1$

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Effect of T on K

13. Calculate ΔG° and the equilibrium constant K at 25°C for the reaction $2 \text{NH}_3(\text{g}) + \frac{5}{2} \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{g})$ using data in Appendix D.

What is the expression for ΔG° in terms of Q and K ?

$\Delta G^\circ = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$

Example: 14.13

$\Delta H^\circ = 2\Delta H_f^\circ(\text{NO}_2, \text{g}) + 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) - 2\Delta H_f^\circ(\text{NH}_3, \text{g})$

$\Delta S^\circ = 2S^\circ(\text{NO}_2, \text{g}) + 3S^\circ(\text{H}_2\text{O}, \text{g}) - 2S^\circ(\text{NH}_3, \text{g}) - \frac{5}{2}S^\circ(\text{O}_2, \text{g})$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\frac{\Delta G^\circ}{RT} = \ln(1/K) = -\ln(K) \Rightarrow K = e^{-\Delta G^\circ/RT}$

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Effect of T on K

$\Delta G^\circ = RT \ln(1/K) = \Delta H^\circ - T\Delta S^\circ$

For values of T near 298 K, ΔH° and ΔS° are nearly constant.

This means the graph of $\ln(K)$ versus $1/T$ is nearly a straight line,

with slope $m = -\Delta H^\circ/R$
 and intercept $b = \Delta S^\circ/R$ at $1/T = 0$ ($T = \infty$)

$-\ln(K) = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$y = mx + b$

Handwritten notes: slope is downward, < 0; $\Delta H^\circ > 0$ endothermic; slope = $-\frac{\Delta H^\circ}{R}$

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[TP] The plot shows how $\ln(K)$ vs $1/T$ for $A \rightleftharpoons B$. The standard enthalpy change of reaction, $\Delta_r H^\circ$, is ...

100% 1. < 0
 0% 2. = 0
 0% 3. > 0
 0% 4. More information is required
 0% 5. Not sure

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$y = mx + b$

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[TP] The plot shows how $\ln(K)$ vs $1/T$ for $A \rightleftharpoons B$. The standard entropy change of reaction, $\Delta_r S^\circ$, is ...

100% 1. < 0
 0% 2. = 0
 0% 3. > 0
 0% 4. More information is required
 0% 5. Not sure

$\ln(K) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$

$\lim_{T \rightarrow \infty} \ln(K) = +\frac{\Delta S^\circ}{R}$

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[TP] The reaction $N_2(g) + 2 H_2(g) \rightleftharpoons 2 N_2H_4(l)$ is endothermic. What temperature range will result in the greatest amount of products? Hint: Sketch $\ln(K)$ vs $1/T$.

0% 1. Very low T
 82% 2. Very high T
 0% 3. The amount will be the same at all T
 0% 4. More information needed
 18% 5. Not sure

$K < 1$

$\frac{\Delta S^\circ}{R} < 0$

How to make K as large as possible.

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Practice: Problem 14.61

$\text{slope} = \frac{\Delta \ln K}{\Delta \left(\frac{1}{T}\right)} = \frac{\ln(K_2) - \ln(K_1)}{\frac{1}{T_2} - \frac{1}{T_1}}$
 $-\frac{\Delta H^\circ}{R} = \frac{\ln(K_2/K_1)}{\frac{1}{T_2} - \frac{1}{T_1}}$
 $\Delta H^\circ = -R \left(\frac{\ln(K_2/K_1)}{\frac{1}{T_2} - \frac{1}{T_1}} \right)$
 $= -57.9 \text{ kJ/mol}$
 $\Delta S^\circ = -178 \text{ J/mol K}$

61. The equilibrium constant at 25°C for the reaction

$$2 \text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$$

6.8. At 200°C the equilibrium constant is 1.21×10^{-3} . Calculate the enthalpy change (ΔH) for this reaction, assuming that ΔH and ΔS of the reaction are constant over the temperature range from 25°C to 200°C.

$\Delta H < 0$
 $\Delta S < 0$

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