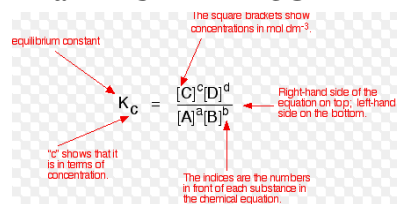
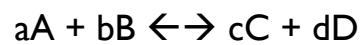


Thermodynamics & Statistical Mechanics

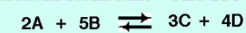
2016



http://www.ck12.org/Book:Phonix_Chemistry/Chemical_Equilibrium/The_Equilibrium_Constant/Calculating_the_Equilibrium_Constant/From_Ab_Equilibrium_Concentrations/Working_Equilibrium_Constant_Expressions/working_solutions_and_answers

The Equilibrium Constant

The Equilibrium Constant– The BIG K



$$K = \frac{[\text{Products}]}{[\text{Reactants}]} \quad K = \frac{[C]^3 [D]^4}{[A]^2 [B]^5}$$

If K is large, then products are favored.
We omit Solids & Liquid Water. They have constant concentrations.

<http://boomeria.org/chemistry/texts/12secondsemss.html>

$\Delta G^\circ = -RT \ln K_{eq}$

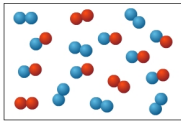
$$K_{eq} = e^{-\Delta G^\circ / RT}$$

$\text{Red} + \text{Blue} \leftrightarrow \text{red-blue}$

$$K_{eq} = RT \ln \frac{[\text{red-blue}]}{[\text{red}][\text{blue}]}$$

$\text{B} + \text{R} \leftrightarrow \text{B-R}$

At equilibrium there are
 3 R-R; 5 B-B and 7 R-B
 K_{eq} is $7/(3)(5)$
 $\Delta G^\circ = -RT \ln(7/15) = 0.45 \text{ kcal/mol}$
 $\Delta G^\circ = -1.36 \log(7/15)$
 Positive so there are more reactant than product at equilibrium



Note: This should be $\text{B} + \text{R} \rightarrow 2\text{B-R}$ (calculate ΔG° for that reaction)

$\Delta G^\circ = -RT \ln K_{eq}$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$K_{eq} = e^{-\Delta G^\circ / RT}$

- What if there were one mole of B, R, and B-R? What would be the ΔG be?
- If there were 3 red; 5 blue and 7 r-b what is ΔG ?

$\text{B} + \text{R} \leftrightarrow \text{B-R}$

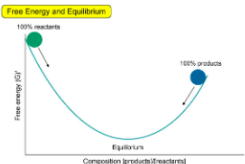
At equilibrium there are
 3 red; 5 blue and 7 R-B
 $\Delta G^\circ = -RT \ln(7/15) = 0.45$

$\Delta G^\circ = -RT \ln K_{eq}$

$$K_{eq} = RT \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$K_{eq} = e^{-\Delta G^\circ / RT}$

$a\text{A} + b\text{B} \leftrightarrow c\text{C} + d\text{D}$



Pure R or P are at high energy (actually they are undefined since they would be $\log(0)$ or $\log(1/0)$)

The equilibrium mixture (K_{eq}) is at the lowest energy.

<https://wikispaces.psu.edu/pages/viewpage.action?pageId=112526687&navigatingVersions=true>

$$\Delta G = \Delta G^\circ + 2.303RT \log_{10} \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

$$\Delta G = \Delta G^\circ + 2.303(1.987 \frac{\text{cal}}{\text{mol}})(298\text{K}) \log_{10} \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

$$\Delta G = \Delta G^\circ + 1.4 \frac{\text{kcal}}{\text{mol}} \log_{10} \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

I will use 1.36 or 1.4 for this constant
 This number depends on T (since it has RT in it)

Standard Free Energy Change

<http://hyperphysics.phy-astr.gsu.edu/hbase/chemical/gibbspon.html>

For biochemical reactions, it is convenient to reference the change in Gibbs free energy ΔG at some standard set of conditions. The conditions usually chosen are listed in the table. The standard value ΔG^0 is determined from experimental data and allows the evaluation of ΔG for other experimental conditions.

Standard Conditions	
• T = 25°C = 298K	
• P = 1 atm	
• [C]=1 M, all reactants	
• Water 55.6M	
• H ⁺ conc = 10 ⁻⁷ M (pH=7.0)	

$\Delta G^0 = -RT \ln K'_{eq}$

The notation ΔG^0 is used for pH=7.0 because ΔG^0 is used for conditions pH = 0.0 or 1 M H⁺.

Relation between ΔG^0 and K'_{eq}	
K'_{eq}	ΔG^0 kcal/mol
10 ⁶	-8.2
10 ⁴	-5.5
10 ²	-2.7
10 ¹	-1.4
10 ⁰	0.0
10 ⁻¹	1.4
10 ⁻²	2.7
10 ⁻⁴	5.5
10 ⁻⁶	8.2

$\Delta G^0 = -RT \ln K_{eq}$

$\Delta G^0 = -1.36 \log K_{eq}$

ΔG^0 Kcal/mol	Keq
13.6	1E-10
12.24	0.00000001
10.88	0.00000001
9.52	0.0000001
8.16	0.000001
6.8	0.00001
5.44	0.0001
4.08	0.001
2.72	0.01
1.36	0.1
0	1
-1.36	10
-2.72	100
-4.08	1000
-5.44	10000
-6.8	100000
-8.16	1000000
-9.52	10000000

$\Delta G^0 = -RT \ln K_{eq}$

$\Delta G^0 = -1.36 \log K_{eq}$

Every step of 1.36 kcal/mol changes the equilibrium constant by 10 fold.

ΔG^0 Kcal/mol	Keq
13.6	1E-10
12.24	0.000000001
10.88	0.00000001
9.52	0.0000001
8.16	0.000001
6.8	0.00001
5.44	0.0001
4.08	0.001
2.72	0.01
1.36	0.1
0	1
-1.36	10
-2.72	100
-4.08	1000
-5.44	10000
-6.8	100000
-8.16	1000000
-9.52	10000000

$\Delta G^0 = -1.36 \log K_{eq}$

Relationship between ΔG^0 and Keq

Every step of 1.36 kcal/mol changes the equilibrium constant by 10 fold.

ΔG^0 Kcal/mol	Keq
13.6	1E-10
12.24	0.000000001
10.88	0.00000001
9.52	0.0000001
8.16	0.000001
6.8	0.00001
5.44	0.0001
4.08	0.001
2.72	0.01
1.36	0.1
0	1
-1.36	10
-2.72	100
-4.08	1000
-5.44	10000
-6.8	100000
-8.16	1000000
-9.52	10000000
-10.88	100000000

$\Delta G^0 = -1.36 \log K_{eq}$

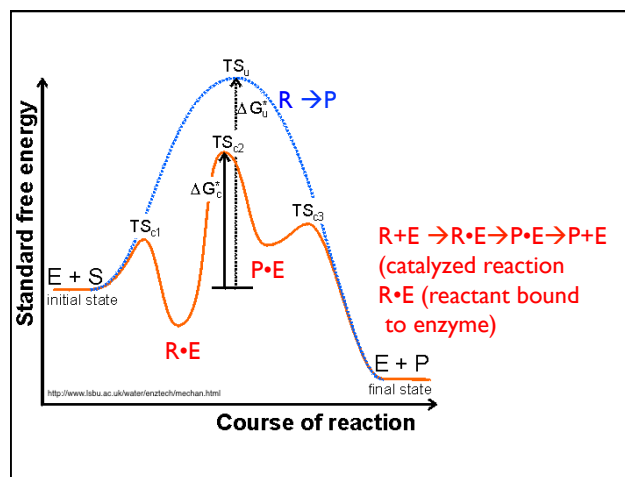
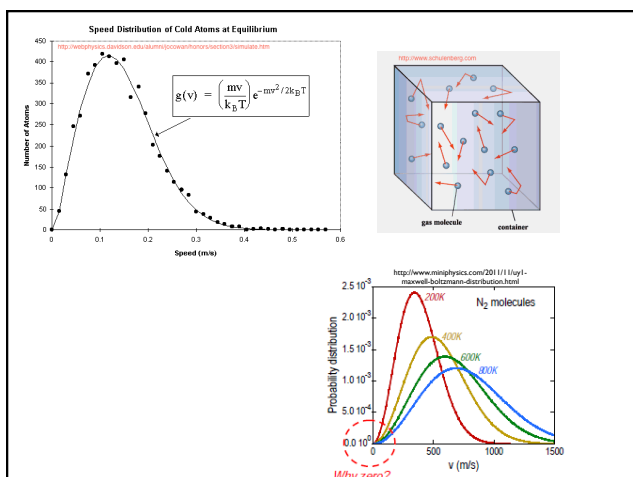
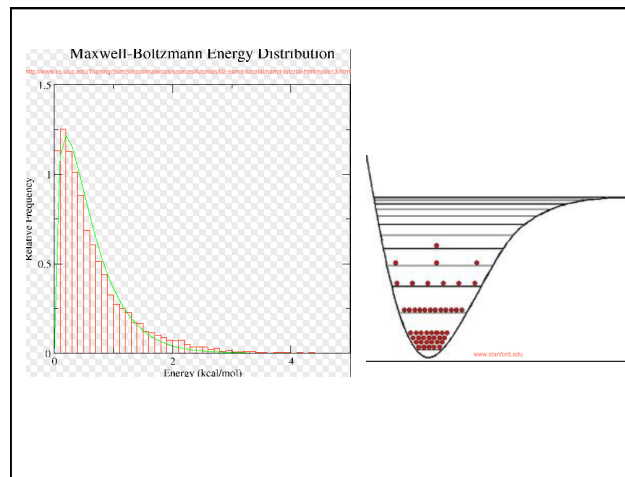
ΔG° Kcal/ mol	K_{eq}
13.6	1E-10
12.24	0.00000001
10.88	0.00000001
9.52	0.0000001
8.16	0.000001
6.8	0.00001
5.44	0.0001
4.08	0.001
2.72	0.01
1.36	0.1
0	1
-1.36	10
-2.72	100
-4.08	1000
-5.44	10000
-6.8	100000
-8.16	1000000
-9.52	10000000
-10.88	100000000

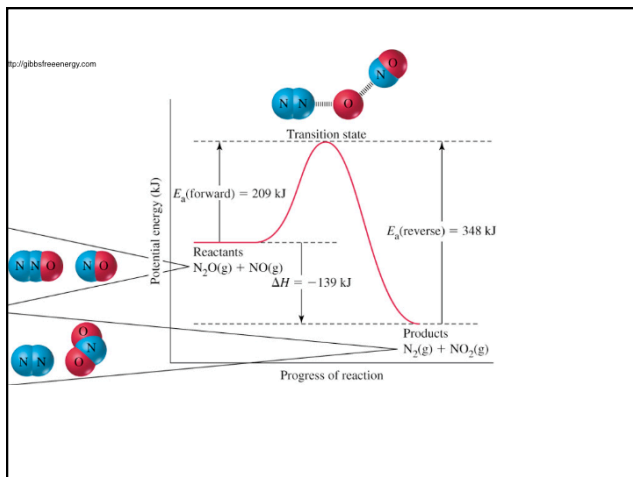
$\Delta G^\circ = -1.36 \log K_{eq}$

If reaction is $A \leftrightarrow B$ what is B/A

If $K_{eq} = 1, 10, 100, 0.1, 0.001$

What is ΔG° ?





What if the P/R ratio does not equal K_{eq} ?

The energy of the system has changed

$$\Delta G = \Delta G^\circ + 1.4 \text{ kcal/mol} \log \frac{[\text{P}]}{[\text{R}]}$$

$$\Delta G = -1.4 \log K_{\text{eq}} + 1.4 \text{ kcal/mol} \log \frac{[\text{P}]}{[\text{R}]}$$

(so $\Delta G = 0$ when $\text{P/R} = K_{\text{eq}}$ (when the concentrations are at equilibrium))

For example $\text{ADP} + \text{P}_i = \text{ATP}$ $K_{\text{eq}} = 10^5$ at pH 7.0

This means

1) The standard free energy of this reaction is:

$$\Delta G^\circ = (-1.36 \text{ kcal/mol}) \log K_{\text{eq}} = (-1.36 \text{ kcal/mol}) \log 10^5 = 6.8 \text{ kcal/mol}$$

The free energy (ΔG) is 0 when $[\text{P}]/[\text{R}] = 10^5$

$$\Delta G = 6.8 + 1.36 \log 10^5 = 0 \text{ kcal/mol}$$

2) If you had 1M of ADP and 1M of Pⁱ and 1M of ATP at pH 7 the system would be out of equilibrium. The free energy available to do work is:

$$\Delta G = \Delta G^\circ + (1.36 \text{ kcal/mol}) \log [1]/[1][1] = + 6.8 \text{ kcal/mol}$$

3) If you have 10^{-2}M Pi the equilibrium ratio of ATP/ADP = 10^{-7} since
 $K_{eq} = 10^{-5} = \text{ATP}/(\text{ADP} * \text{Pi})$

4) However, ATP/ADP = 10^3 in the cell. How much work must be done to achieve this concentration ratio (if there is 10^{-2}M Pi)?

$$\begin{aligned}\Delta G &= \Delta G^\circ + (1.36\text{kcal/mol}) \log[\text{ATP}]/[\text{ADP}][\text{P}_i] \\ &= 6.8 \text{ kcal/mol} + 1.36 \log [10^3]/10^{-2} = 13.6 \text{ kcal/mol}\end{aligned}$$