5.111 Lecture Summary #16 Wednesday, October 15, 2014

Readings for today: Section 8.1 (Section 7.1 in 4th *ed*) – Spontaneous Change, Sections 8.2 and 8.8 (Sections 7.2 and 7.8 in 4th *ed*) - Entropy, Sections 8.12, 8.13, 8.15 (Sections 7.12, 7.13, 7.15 in 4th *ed*) – Free Energy.
Reading for Lecture #17: Section 8.16 (Section 7.16 in 4th *ed*) – Free-Energy Changes in Biological Systems.

Topics: **Thermodynamics**
- **I.** Spontaneous change and free energy
- **II.** Entropy
- **III.** Free energy of formation

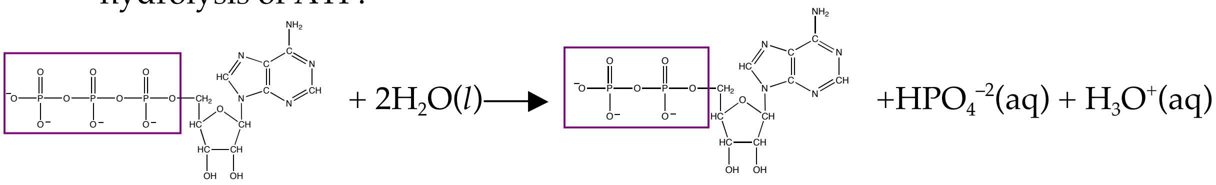
I. SPONTANEOUS CHANGE AND FREE ENERGY

A **spontaneous change** is a process that, given enough time, occurs without the need for outside intervention.

For example, the following reactions are spontaneous at constant pressure:

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ $\Delta H° =$ ____________ kJ/mol

hydrolysis of ATP:



$+ 2H_2O(l) \longrightarrow$ $+ HPO_4^{-2}(aq) + H_3O^+(aq)$

___________ (aq) ___________ (aq) $\Delta H° =$ _________ kJ/mol

But so are these …

$H_2O(s) \rightarrow H_2O(l)$ $\Delta H° = +6.95$ kJ/mol
$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$ $\Delta H° = +28$ kJ/mol

Is ΔH the key to spontaneity? __________!

Condition for spontaneity under constant P + T involves GIBBS FREE ENERGY, ΔG.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

where T = temperature and ΔS = change in entropy, a measure of disorder.

$\Delta G < 0$ ________________________ process
$\Delta G > 0$ ________________________ process
$\Delta G = 0$ equilibrium

Under constant pressure and temperature, a process is spontaneous when $\Delta G < 0$, not necessarily when $\Delta H < 0$.

Figuring this out was one of the towering achievements of thermodynamics!!

For example, $NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

$\Delta H_r° = +28.\ kJ/mol$ $\Delta S_r° = +109.\ JK^{-1}mol^{-1}$

$\Delta G° = \Delta H° - T\Delta S°$

at T = 298. K, $\Delta G°$ = + 28. kJ/mol - 298. K (__________________)

$\Delta G°$ = + 28. kJ/mol – $32.\underline{4}8$ kJ/mol

$\Delta G°$ = __________ kJ/mol

$\Delta G°$ is negative, even though $\Delta H°$ is positive. The reaction is **spontaneous**.

Now consider glucose oxidation at room temperature:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\Delta H° = -2{,}816\ kJ/mol, \quad \Delta S° = +233\ J/K{\bullet}mol$$

$\Delta G°$ = –2,816 kJ/mol – 298 K(__________________________) = -2,885 kJ/mol

$\Delta G°$ more negative than $\Delta H°$. This reaction is spontaneous at ____________________ temperatures.

II. ENTROPY

Entropy, S, is a measure of the __________________ of a system .
ΔS = change in entropy. ΔS is a state function.

$\Delta S°$ positive ⇒ _________________ in disorder

$\Delta S°$ negative ⇒ ________________ in disorder

Disorder of gas _____ liquid _____ solid
In solids, molecules cannot move around freely.

Internal degrees of freedom and internal motions – e.g. vibrations- also contribute to entropy

Without calculations, we can predict the sign of ΔS for many reactions. For example,

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ is predicted to have a ____________________ ΔS.

Demo: Let's "watch" entropy increase as liquid turns to gas. We will mix $H_2O_2\,(l)$ with food color and soap (to help us "watch" $O_2\,(g)$ bubble), and use yeast diluted in water to speed up the reaction.

Entropy for reactions, ΔS_r°

can be calculated from **absolute** entropies of products and reactants,

$$\Delta S_r^{\circ} = \Sigma S^{\circ}(\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_) - \Sigma S^{\circ}(\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_)$$

where S° is the absolute standard entropy.

S has an absolute zero – the perfect crystal at T = 0 K (perfectly ordered, no disorder).

For example, consider the decomposition of hydrogen peroxide.

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

$\Delta S_r^{\circ} = \Sigma S^{\circ}(\text{products}) - \Sigma S^{\circ}(\text{reactants})$

$\Delta S^{\circ} = \_\_\_\_ S^{\circ}(\_\_\_\_\_\_\_\_\_\_\_\_) + S^{\circ}(\_\_\_\_\_\_\_\_\_\_) - \_\_\_\_ S^{\circ}(\_\_\_\_\_\_\_\_\_\_)$

$\Delta S^{\circ} = 2(70.\ JK^{-1}mol^{-1}) + (205\ JK^{-1}mol^{-1}) - 2(110.\ JK^{-1}mol^{-1})$

$\Delta S^{\circ} = \_\_\_\_\_\_\_\_\_\_\_\_\ JK^{-1}mol^{-1}$

Why is ΔS° positive? The reaction converts liquid → liquid and gas.

But is reaction spontaneous at room temperature?

$$\begin{aligned}\Delta G^{\circ} &= \Delta H^{\circ} - T\Delta S^{\circ} \\ &= -196\ kJ/mol - 298.15\ K\ (\_\_\_\_\_\_\_\_\_\_\_\_\ kJ\ K^{-1}mol^{-1}) \\ &= -233\ kJ/mol \qquad \text{(The reaction is } \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \text{)}\end{aligned}$$

Now consider ice melting at 298.15 K. $H_2O(s) \rightarrow H_2O(l)$

$\Delta S^{\circ} = S^{\circ}(\_\_\_\_\_\_\_\_\_\_\_\_) - S^{\circ}(\_\_\_\_\_\_\_\_\_\_\_\_) = 69.91 - 41.32$ $\quad \Delta S^{\circ} = 28.59\ J\ K^{-1}\ mol^{-1}$

Why is $\Delta S^{\circ} > 0$? ________________________

$\Delta G^{\circ} = 6.95 - 298.15K(2.859 \times 10^{-2}\ kJ/K\ mol) = -1.57\ kJ/mol$

Ice melting is spontaneous at room temperature even though ΔH° is positive.

III. FREE ENERGY OF FORMATION, ΔG_f

analogous to ΔH_f

ΔG_f^o ≡ standard Gibbs free energy of formation

≡ ΔG_r^o for formation of 1 mol of compound from its elements in their most stable form in the standard states at P = 1 bar and T = 298.15 K.

Tabulated for many compounds like ΔH_f^o, but can also be calculated from

$$\_\_\_\_\_\_\_\_ = \_\_\_\_\_\_\_\_ - T\Delta S^\circ$$

For example,

$C(gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta G^\circ = -394.36 \text{ kJ/mol} = \Delta G_f^o$

ΔG_f^o is important because it is a measure of a compound's stability relative to its elements.

If $\Delta G_f^o < 0$, a compound is thermodynamically ____________________ relative to its elements.

If $\Delta G_f^o > 0$, a compound is thermodynamically ____________________ relative to its elements.

Free energy tells whether or not a reaction will happen spontaneously, but it tells us ______________________ about the rate of the reaction (for rate information we need kinetics).

To calculate ΔG° for a reaction…

$$\Delta G_r^\circ = \Sigma\Delta G_f^\circ(\text{products}) - \Sigma\Delta G_f^\circ(\text{reactants})$$

$$\text{OR} \quad \Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

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