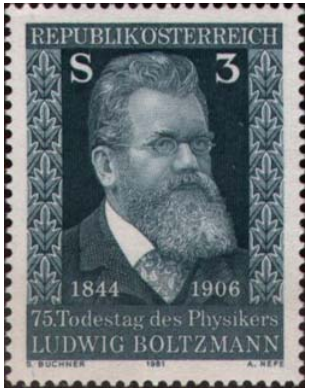
Chapter 19 – Entropy



Molecular Properties of Entropy (1st & 2nd Laws of Thermo)

The Magnitude of Entropy Grows with Number of Microscopic States:

(1) $S^o(g) > S^o(l) > S^o(s)$

(2) Molar Entropy of a molecule increases with complexity and temperature

(3) Spreading of Energy and/or Molecules increases S

Thermodynamic and Statistical Definitions of Entropy (0th, 1st, 2nd, 3rd Laws of Thermo)

(1) Thermodynamic: $\Delta S = q_{rev}/T$

(2) Statistical: $S = k_B \ln W$ (W is the number of configurations), S is 0 at 0 K and S increases with T (S is always positive)

(3) $\Delta S^o_{sys} = \Sigma[S^o(\text{products})] - \Sigma[S^o(\text{reactants})]$

(4) $\Delta S^o_{surr} = -\Delta H^o_{sys}/T$

(5) $\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta S^o_{sur}$; $\Delta S^o_{uni} > 0$ (spontaneous)

(6) Equilibrium Condition of a Phase Change: Ice is Stable below 0 °C; not above 0 °C

A Calculation of ΔS_{uni}, The Definition of ΔG_{sys}, Calculations with ΔG_{sys}, ΔH_{sys} & ΔS_{sys}

(1) ΔG^o_{rxn}, Chemical Reactions at Standard Conditions: Propane Example

(2) Definition of ΔG as a State Variable, $\Delta H - T\Delta S$

(3) Calculations with ΔG

(a) As a State Variable, $\Delta H - T\Delta S$

(b) T-Dependence: (i) $\Delta H > 0$ $\Delta S > 0$, (ii) $\Delta H < 0$ $\Delta S < 0$, (iii) $\Delta H > 0$ $\Delta S < 0$, (iv) $\Delta H < 0$ $\Delta S > 0$

(c) For Cases (i) and (ii), T at which the process becomes Spontaneous/Nonspont.

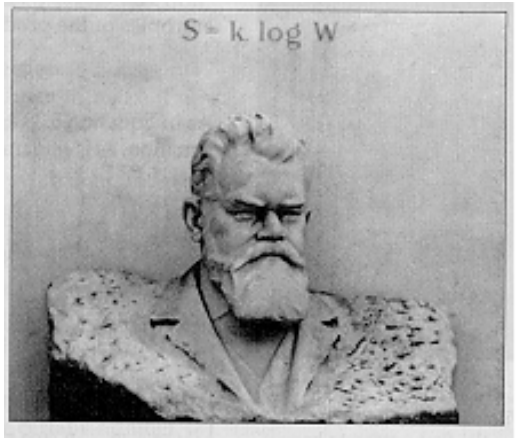
ΔG^o and K, ΔG and Q

(1) $\Delta G = \Delta G^o + RT\ln Q$

(2) Q = 1 when all products and reactants are at standard state

(3) $\Delta G = \Delta G^o$

(4) At Equilibrium $\Delta G = 0$ and $Q = K$, $\Delta G^o = -RT\ln K$



Help/Review Sessions

Mon Dec 11th 3.35-5:00 PM, LGRT 103

Mon Dec 11th 7:15-8:45 PM, Here

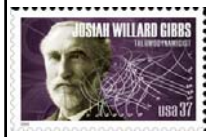
Mon Dec 18th 3:35-5:00 PM, Goessmann 51

Mon Dec 18th 7:15-8:45 PM, Here

Gibbs Energy: G = H – TS

A State Function of the System that Predicts Spontaneity

For an Isothermal Process, Initial → Final State: $\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$



$$\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta S^o_{sur}$$

$$\Delta S^o_{uni} = \Delta S^o_{sys} + \Delta H^o_{sur}/T$$

$$-T\Delta S^o_{uni} = -T\Delta S^o_{sys} + \Delta H^o_{sys}$$

Rename "$-T\Delta S^o_{uni}$" as ΔG^o_{sys}

$$\Delta G^o_{sys} = \Delta H^o_{sys} - T\Delta S^o_{sys}$$

The process does not have to be at standard state:

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

$\Delta G < 0$ spontaneous, $\Delta G > 0$ nonspontaneous, $\Delta G = 0$ equilibrium

Tips on Calculating ΔS^o, ΔH^o, ΔG^o From Tabulated Values

(1) Use the form of the compound specified in the process (gas, liquid, or solid)

(2) Account for the reaction stoichiometry

(3) Scale ΔS^o, ΔH^o and ΔG^o appropriately to account for the amount transformed

$$\Delta G^o_{rxn} = \Delta H^o_{rxn} - T\Delta S^o_{rxn}$$

or

$$\Delta G^o_{rxn} = \Sigma[\Delta G^o_f(products)] - \Sigma[\Delta G^o_f(reactants)]$$

$$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 4H_2O\ (g) + 3CO_2\ (g)$$

Compound	ΔH^o_f (kJ/mol)	ΔG^o_f (kJ/mol)	S^o (J/K·mol)
C_3H_8 (*g*)	-103.8	-23.5	269.9
CO_2 (*g*)	-393.5	-394.4	213.7
H_2O (*l*)	-285.8	-237.1	69.9
H_2O (*g*)	-241.8	-228.6	188.8
O_2 (*g*)	0	0	205.1

$$\Delta G^o_{rxn} = [4\Delta G^o_f(H_2O,g) + 3\Delta G^o_f(CO_2,g)] - [\Delta G^o_f(C_3H_8,g) + 5\Delta G^o_f(O_2)]$$

$$\Delta G^o_{rxn} = [4(-228.6) + 3(-394.4)] - [(-23.5) + 0] = -2074.1\ kJ$$

$\Delta G = \Delta H - T\Delta S$ is also valid for processes that are not carried out at standard state conditions:

(a) Standard State:

$$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 4H_2O\ (g) + 3CO_2\ (g)$$

$P_{C3H8} = 1$ atm $\quad P_{O2} = 1$ atm $\quad P_{H2O} = 1$ atm $\quad P_{CO2} = 1$ atm

$\Delta G = \Delta G^o + RTlnQ$

$\Delta G = \Delta G^o + RTln[(1)^4(1)^3]/[(1)^5(1)] = \Delta G^o = -2074.1$ kJ

(b) Nonstandard State (one example):

$$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 4H_2O\ (g) + 3CO_2\ (g)$$

$P_{C3H8} = 0.1$ atm $\quad P_{O2} = 0.1$ atm $\quad P_{H2O} = 0.1$ atm $\quad P_{CO2} = 0.1$ atm

$\Delta G = \Delta G^o + RTlnQ = \Delta G^o + RTln[(0.1)^4(0.1)^3]/[(0.1)^5(0.1)] = \Delta G^o + RTln[(0.10)]$

$\Delta G = -2074.1$ kJ + (0.008314 kJ/(mol K))(298)ln[0.1] = - 2074.1 - 5.7 = -2079.8 kJ

The Propane Combustion Process:

$$C_3H_8\ (g) + 5O_2\ (g) \rightarrow 4H_2O\ (g) + 3CO_2\ (g)$$

$P_{C3H8} = 1$ atm $P_{O2} = 1$ atm $P_{H2O} = 1$ atm $P_{CO2} = 1$ atm

$$\Delta G = \Delta G^o + RT\ln Q$$

The Propane Combustion Equilibrium:

$$C_3H_8\ (g) + 5O_2\ (g) \rightleftarrows 4H_2O\ (g) + 3CO_2\ (g)$$

$$0 = \Delta G^o + RT\ln K_e$$

$$\Delta G^o = -RT\ln K_{eq} \qquad K_{eq} = exp[-\Delta G^o/RT]$$

From K_{eq}, the energy balance at standard state (ΔG^o) can be determined.

With a value for ΔG^o, K_{eq} can be calculated.

$$\Delta G^o = -RT\ln K_{eq} \qquad K_{eq} = exp[-\Delta G^o/RT]$$

ΔG^o (kJ)	K_{eq} (at 298 K)
-25.0	2.4×10^4
-10.0	56
-5.0	12
0.0	1
5.0	0.084
10.0	0.018
25.0	4.2×10^{-5}

K_{eq} changes rapidly as a function of ΔG^o

ΔG and Reaction Equilibria

(1) $\Delta G = \Delta G^o + RT\ln Q$

Gibbs energy changes at nonstandard conditions.
$\Delta G < 0$, spontaneous; $\Delta G > 0$ nonspontaneous.

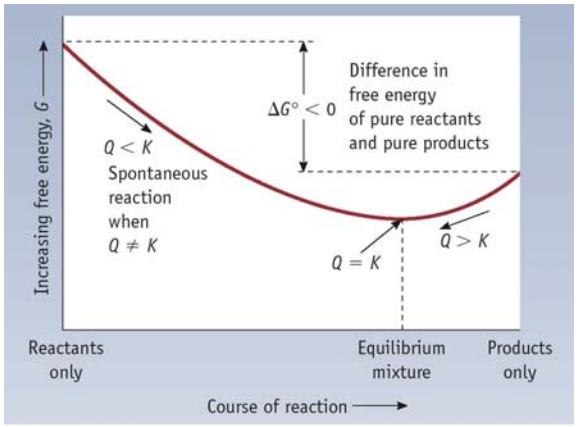
(2) $\Delta G = \Delta G^o$, when $Q = 1$

This corresponds to specific situations in which processes are (imagined) to occur at standard state.

(3) $\Delta G^o = -RT\ln K$, when $\Delta G = 0$

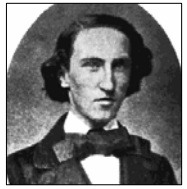
When $\Delta S_{uni} = 0$, the system is at equilibrium.
ΔG (= $-T\Delta S_{uni}$) is also zero under these conditions.

$\Delta G = \Delta G^0 + RT\ln Q$



Chemistry and Life

Josiah Williard Gibbs (1839-1903)



Non spontaneous

Glucose + O_2 → **CO_2 + H_2O**

spontaneous

ΔG^0 = -2880 kJ