

Thermodynamics: Spontaneity and Chemical Equilibrium: Student Review Notes

At constant temperature and pressure, the **Second Law of Thermodynamics** can be written as:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \quad \text{and} \quad \Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \frac{-\Delta H}{T} \geq 0$$

Multiplying both sides by $-T$, and noting that multiplying by a negative number reverses the sense of the inequality, yields

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S_{\text{sys}} \leq 0$$

Multiplication of ΔS_{univ} by $-T$ puts the entropy term in units of energy (J/mol) rather than units of entropy (J/mol K). The system-oriented function $-T\Delta S_{\text{univ}}$ is called the Gibbs Free Energy, ΔG named in honor of J. Willard Gibbs, one of fathers of modern thermodynamics. The Second Law then becomes:

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

The Second Law says that $\Delta S_{\text{univ}} > 0$ for a spontaneous process and that $\Delta S_{\text{univ}} = 0$ for a system at equilibrium. Since absolute temperature, T is always positive, $-T\Delta S_{\text{univ}}$ will be negative for a spontaneous process or $\Delta G < 0$ indicates spontaneity and $\Delta G = 0$ indicates a system at equilibrium. In terms of the applicability of what you learn in a chemistry class to life at large, this is a pretty profound equation. It shows that natural systems have a tension between energy (ΔH is heat energy) and randomness (ΔS). For any natural or man-made system, from a government to an economy to a corporation, it is wise to take into account both energy and entropy. This is the yin and yang of the natural world.

In summary

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

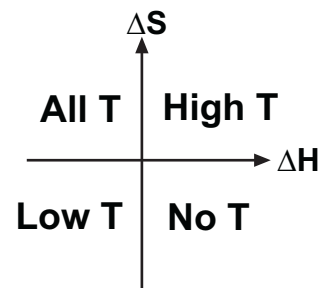
$\Delta G < 0$ indicates that a **chemical reaction is spontaneous**

$\Delta G = 0$ indicates that a **reaction is at equilibrium**

$\Delta G > 0$ Indicates that the **reverse reaction is spontaneous**

The **sign** of ΔH and ΔS can tell you a lot about the spontaneity of a reaction. Remember that exothermic means ΔH is negative, endothermic means ΔH is positive and you can generally tell the sign of ΔS from the phase changes associated with a reaction.

<u>sign of ΔH</u>	<u>sign of ΔS</u>	<u>sign of ΔG</u>	<u>spontaneous as written</u>
-	+	-	yes
+	-	+	NO; reverse is spontaneous
+	+	+ or -	avored at high temp
-	-	+ or -	avored at low temp



Calculation of ΔG

1) Calculation of ΔG from tabulated ΔH° and ΔS° data.

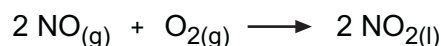
You can clearly see from the equation $\Delta G = \Delta H - T\Delta S$ that the change in Gibbs Free Energy is dependent on temperature. The dependence is right there as a variable.

The question is, how can we use ΔH° and ΔS° data, data taken at 1 atm., 1 M concentrations and typically at 298 K, to calculate a quantity that has temperature dependence?

The answer is that we accept some amount of error in the calculation and recognize that in actuality, ΔH° and ΔS° don't vary a lot with temperature.

We therefore can use standard state tabulated data of enthalpies of formation and absolute entropies to calculate a value for ΔG° .

Example calculation: From the given data, calculate ΔG° for the reaction shown at 298 K.



ΔH°_f (kJ/mol)	90	0	34	$\Delta H^\circ_{\text{rxn}} = 2(34 \text{ kJ/mol}) - 2(90 \text{ kJ/mol}) = -112 \text{ kJ/mol}$
S°_f (J/mol K)	211	205	240	$\Delta S^\circ_{\text{rxn}} = 2(240 \text{ J/mol K}) - [2(211 \text{ J/mol K}) + 205 \text{ J/mol K}] = -112 \text{ kJ/mol}$

$$\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}} = -112 \text{ kJ/mol} - 298 \text{ K} (-.147 \text{ kJ/mol K}) = -68 \text{ kJ/mol}$$

↑
watch your units here

So $\Delta G < 0$ indicates that this reaction is spontaneous in the forward direction at 298 K.

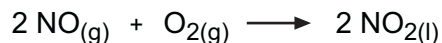
In this example, both ΔH° and ΔS° are negative. Another interesting calculation therefore is the temperature at which the reaction is in equilibrium and above which, the reverse reactions becomes spontaneous.

At equilibrium $\Delta G = 0$:

$$0 = \Delta H^\circ_{\text{rxn}} - T_{\text{eq}}\Delta S^\circ_{\text{rxn}} \quad T_{\text{eq}} = \Delta H^\circ_{\text{rxn}}/\Delta S^\circ_{\text{rxn}} = (-112 \text{ kJ/mol})/(-.147 \text{ kJ/mol K}) = 762 \text{ K}$$

Above this temperature, ΔG will be positive and therefore the reverse reaction will be spontaneous

2) Calculation of ΔG from tabulated standard free energy of formation data. This is just like using heat of formation data and just as in the case of ΔH°_f , pure elemental species in their most stable state have a value of 0.



ΔG°_f (kJ/mol)	87	0	52	$\Delta G^\circ_{\text{rxn}} = 2(52 \text{ kJ/mol}) - 2(87 \text{ kJ/mol}) = -70 \text{ kJ/mol}$
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Gibbs Free Energy and Equilibrium

The change in Gibbs Free Energy and the equilibrium constant are related by the equation:

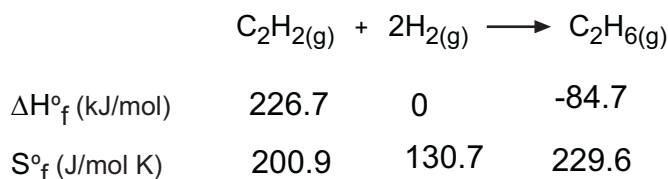
$$\Delta G = \Delta G^\circ + RT \ln Q_C$$

where R is 8.31 J/mol·K and Q_C is the reaction quotient. $\Delta G = 0$ is the condition for equilibrium and the equation reduces to:

$$0 = \Delta G^\circ + RT \ln K_C$$

$$\Delta G^\circ = -RT \ln K_C \text{ or } K_C = e^{-\Delta G^\circ/RT}$$

These equations are super-important. They relate tabulated thermodynamic data to the value of an equilibrium constant. Here is an example that ties together thermodynamics and equilibrium: Given the following thermodynamic data, is the following reaction spontaneous at 298 K and what is the value of the equilibrium constant at 298 K?



1) Is the reaction spontaneous, i.e calculate ΔG

$$\Delta H^\circ_{rxn} = 1(-84.7 \text{ kJ/mol}) - [(226.7 \text{ kJ/mol}) + 0] = -311.4 \text{ kJ/mol}$$

$$\Delta S^\circ_{rxn} = (229.6 \text{ J/mol K}) - [(200.9 \text{ J/mol K}) + 2(130.7 \text{ J/mol K})] = -232.7 \text{ J/mol K}$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn} = -311.4 \text{ kJ/mol} - 298 \text{ K} (-0.2327 \text{ J/mol K}) = -242.1 \text{ kJ}$$

$\Delta G < 0$ and therefore at 298 K the reaction is spontaneous.

2) Calculate the equilibrium constant at 298 K.

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

$$K_C = e^{(-232,100 \text{ J})/(8.314 \text{ J/mol K})(298 \text{ K})}$$

$$K_C = 2.74 \times 10^{42}$$