

Chemical Thermodynamics

Chemical thermodynamics involves the thermodynamic description of systems that are subject to chemical change.

Four principals of thermodynamics:

Zeroth Law: There is an absolute temperature scale, T.

All bodies have some measure of hotness (temperature).

If bodies A and B are in thermal equilibrium with a third body C, then they are also in thermal equilibrium with each other.

First Law: Conservation of Energy, that energy can neither be created or destroyed.

Internal Energy is a state function of a system.

It can be changed by a heat transfer to the system or by work done by the system.

The overall change in internal energy is independent upon the path taken to change the state.

Second Law: Entropy is a state function of the system.

A change in the entropy of a system is related to a heat transfer:

$$dS_{\text{sys}} = dq/T,$$

where dq is a transfer of heat to the system.

For an irreversible system $dq/T < dS_{\text{sys}}$, and entropy always increases

For a reversible system we must consider the system and its surrounding universe

$$dS_{\text{univ}} = dS_{\text{sys}} + dS_{\text{surr}} = 0$$

Third Law: The entropy of a body is zero at T=0.

At 0° K, most substances are at their most ordered, and therefore the entropy of crystalline solids at 0° K is taken to be zero (S=0).

Often in aqueous systems we are dealing with changes in chemical compositions, such as the changes in the number of moles of a species resulting from a chemical reaction or a transfer between phases (water-rock interactions or gas exchange).

Chemical reactions move toward equilibrium. Using chemical thermodynamics we

can ask what is the state of a system, say a three phase system of calcite, carbon dioxide and water. Is this system far from or close to equilibrium?

A system at equilibrium is characterized by being in a state of minimum energy.

For systems that are at constant temperature (T) and pressure (P), the appropriate measure of energy is Gibbs free energy (G), which is related to enthalpy (H) or heat, and entropy (S) by the equation:

$$G=H-TS$$

Where, T is temperature in degrees Kelvin.

Enthalpy (H) is the heat content of a substance at constant pressure [kJ/mol, kcal/mol],

Entropy (S) is a measure of the randomness or disorder of a phase [kJ/mol.K; kcal/mol.K]

Gibbs free energy (G) has units of [kJ/mol, kcal/mol].

Free energy cannot be measured directly, but we can estimate the difference (ΔG) between free energies of substances in a reaction.

For changes in G at constant T and P we can write the above reaction as:

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

When a system moves toward equilibrium it may release heat, its entropy may increase, or some combination of heat and entropy may change to cause a net decrease in G.

Thus ΔG is negative for a spontaneous process,
 $\Delta G=0$ for processes at equilibrium.

Appendix II in your text book lists the standard free energies of formation (ΔG_f°) of various species-solids, liquids, gases, and solutes.

They represent the free energy change when 1 moles of a species in its standard state is formed from the elements of which it is composed, with the elements all being in their standard states.

The standard state is commonly taken to be the pure substance at the same temperature and pressure as the solution of interest.

The standard free energy of formation of calcite (CaCO_3) is -1129.07 kJ/mole and represents the energy change when 1 mole of calcite at 25°C and 1 atm is formed from 1 mole of metallic calcium, 1 mole of graphite, and 1.5 moles of O_2 , all at 25°C and 1 atm.

) G_{fcaCO_3} is negative, indicating that energy is released when formed from its elements.

By convention, the standard free energies of formation of elements in their standard states is zero, for example C graphite, Fe metal, H_2 gas, O_2 gas, N_2 gas.

By definition, standard free energy of formation of the hydrogen ion H^+ is zero, and the standard free energies of formation of all the other ions in solution is based on this.

Let's consider two vessels, one containing 100 % nitrogen gas and the other containing 100% argon gas.

A valve between the two vessels is opened and the two gases will now mix on their own, by diffusion, until each vessel contains 50 % nitrogen and 50% argon.

In this example, no heat was transferred and no work was done.

The gases mixed in order to form a more disordered state.

In this example, the entropy term is the most important.

With changes of state from solid to liquid to gas, entropy increases discontinuously with increasing disorder of the phase.

For instance:

$$\begin{aligned} S(\text{ice}) &< S(\text{water}) < S(\text{steam}) \\ 10.68 &< 16.72 < 45.11 \text{ cal/mol K} \\ 44.68 &< 69.95 < 188.73 \text{ J/mol/ K} \end{aligned}$$

The standard enthalpy of formation (ΔH_f°) represents the heat change when 1 mole of a species is formed from its constituent elements, with everything being in its standard state.

The enthalpy (ΔH) of formation of an element is defined at 1 bar pressure and 25 °C (298.15K), ΔH is defined as zero for the most stable form of the element. For example, the most stable form of sulfur at 1 bar and 25°C is rhombic sulfur and its $\Delta H=0$.

Monoclinic sulfur is unstable relative to the rhombic form and has $\Delta H=0.2971$ kJ/mol at 1 bar and 25°C.

The enthalpy of a reaction is the heat transfer between a system and its surroundings for a process at constant pressure, but not constant temperature or volume.

Let's take the reaction between gaseous hydrogen and gas to make liquid water at 25 °C.

	$\text{H}_2(\text{g})$	$+ \frac{1}{2} \text{O}_2(\text{g})$	$= \text{H}_2\text{O}(\text{l})$	
Enthalpy (H):	0	0	-285.83 kJ/mol	
Volume (V):	24.5L	12.3 L	0.018 L	

The changes in the enthalpy and volume for this reaction are:

$$\Delta H_r = -285.83 - 0 - 0 = -285.83 \text{ kJ/mol}$$

$$\Delta V_r = 0.018 - 24.5 - 12.3 = -36.8 \text{ L}$$

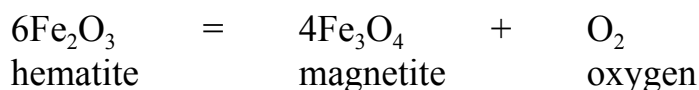
The negative sign for ΔH_r means that the reaction is exothermic (gives off heat, temperature rises).

A positive ΔH_r refers to endothermic reactions (system cools as the reaction progresses).

The large negative volume change means that the reaction can be explosive.

ΔG , ΔH , ΔS are all calculated in the same way.

Let's use the reaction between hematite, magnetite, and oxygen



First, for every chemical reaction you need to check that it is balanced.
 On the left side of the equation there are $6 \times 2 \text{ Fe} = 12 \text{ Fe}$ and $6 \times 3 \text{ O} = 18 \text{ O}$.
 On the right side there are $4 \times 3 = 12 \text{ Fe}$ and $4 \times 4 = 16 + 2 = 18 \text{ O}$.
 So the equation is balanced.

We calculate ΔG , ΔH , and ΔS by taking the sum of the products (appearing on the right hand side of the equation) minus that of the reactants (species on the left side of the equation). The ΔG , ΔH , and ΔS for each species is the formation multiplied by its coefficient in the chemical reaction.

	ΔG_f°	ΔH_f°	S°
	kJ/mol	kJ/mol	kJ/mol K
hematite	-742.8	-824.7	87.7×10^{-3}
magnetite	-1012.9	-1116.1	205.0×10^{-3}
oxygen	0	0	60.4×10^{-3}

$$\Delta G_R^\circ = 4 \times (-1012.9) + 0 - 6 \times (-742.8) = +202.6 \text{ kJ/mole}$$

$$\Delta H_R^\circ = 4 \times (-1116.1) + 0 - 6 \times (-824.7) = +241.9 \text{ kJ/mole}$$

$$\Delta S_R^\circ = 4 \times (205.0 \times 10^{-3}) + 60.4 \times 10^{-3} - 6 \times 87.7 \times 10^{-3} = -131.6 \times 10^{-3} \text{ kJ/mol K}$$

at $T = 298.15 \text{ K}$ (25°C)

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

$$+202.6 \text{ kJ/mole} = +241.9 \text{ kJ/mole} - (298.15 \text{ K} \times -131.6 \times 10^{-3} \text{ kJ/mol K})$$

A quantity closely related to G is the chemical potential (μ_i), which is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P}$$

where,

i refers to a particular component in the system, and

n is the number of moles of that component being added to the system.

The chemical potential μ_i is the partial molar Gibbs free energy or the amount (per mole) by which the Gibbs free energy of the system changes with the addition of an infinitesimal amount of a particular component.

For a one component system, the chemical potential μ_i of a the Gibbs free energy per mole.

Consider a system with two phases, A and B. (Ice and water).

If $\mu_i^A > \mu_i^B$, then the transfer of some component I from A to B will result in a release of energy (ΔG is negative).

If $\mu_i^A = \mu_i^B$, then $\Delta G = 0$ and the system is at equilibrium.

In this example the phases A and B can be gas-liquid, gas-solid, liquid-liquid, liquid-solid, or solid-solid

Other quantities related to G include activity a and fugacity f .

Activity a , is considered as an effective concentration for liquids and solids, while, fugacity f is an effective pressure for gases.

You can also think of the activity a of a substance as a fraction of the total concentration that participates in reactions. Typically, activity a is less than the concentration.

If always present during a reaction (always in excess), the activities of pure solids and liquids may be assumed to be unity, or $a_i = 1$.

For solid or liquid mixtures, we can define ideal solutions for which $a_i = N_i$, the mole fraction of i in the mixture.

For a two-component system (binary system) the mole fraction of component 1 in a solution with component 2 is given by:

$$N_1 = \frac{n_1}{n_1 + n_2}$$

where,

n_1 and n_2 are the number of moles of the respective components in a given volume of solution.

Let's say we have a CaCO_3 - MgCO_3 solid solution that contains 5 weight percent Mg. What is the mole fraction of MgCO_3 in the solid solution?

Don't be confused by the term solid solution. Solution is referring to a mixture of two components that are in the solid phase. In this example the two solids are calcium carbonate and magnesium carbonate that combine to form a low-Mg calcite.

A mixture of two components in a liquid phase would be called an aqueous solution.

The formula weights of Mg, Ca, and CO_3 are 24, 40 and 60, respectively.

$$\text{The Wt\% of MgCO}_3 = [5 \times (24+60)]/24 = 17.5$$

$$\text{The Wt\% of CaCO}_3 = 100-17.5 = 82.5$$

$$\text{The relative number of moles of MgCO}_3 \text{ is } 17.5/84=0.21$$

$$\text{The relative number of moles of CaCO}_3 \text{ is } 82.5/100=0.825$$

$$\begin{aligned} \text{Mole fraction of MgCO}_3 &= \text{moles MgCO}_3 / (\text{moles MgCO}_3 + \text{moles CaCO}_3) \\ &= 0.21 / (0.21 + 0.825) = 0.20 \end{aligned}$$

The chemical potential of component i , can be expressed as :

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

$$\mu_i = \mu_i^\circ + RT \ln f_i$$

where, μ_i° is a constant which is the chemical potential of component i in its standard state,

R is the gas constant (8,314.3 J/mol K; 1.98717 cal/mol K)

T is temperature in Kelvin.

The standard state is commonly taken to be the pure substance at the same temperature and pressure as the solution of interest.

Thus for aqueous solutions, $a_{\text{H}_2\text{O}} = a_{\text{H}_2\text{O}}^\circ$ and $a_{\text{H}_2\text{O}} = 1$ when the solution is infinitely dilute. But can be assumed to be equal to 1 for waters with TDS levels (as NaCl) below 9000 mg/L.

For solutes in aqueous solutions, the activity approaches its concentration as the concentration of the dissolved solute approaches zero:

$$a_i \approx m_i \text{ as } m_i \rightarrow 0.$$

where, m_i is the molal concentration of component i in the aqueous solution.

The ratio of an activity to a component to its molal (moles of i in 1 kg of water) concentrations is the activity coefficient: γ_i , where, $\gamma_i = a_i/m_i$

and hence, $\gamma_i \approx 1$ as $m_i \rightarrow 0$.

Typically, γ_i is less than 1 for ions and greater than 1 for molecular or neutral species such as $\text{CO}_2(\text{aq})$ and silicic acid (H_4SiO_4).