MSE-204 Thermodynamics for Materials Science

L10 REACTING SYSTEMS

REACTIONS IN THE GAS PHASE | CONDITIONS FOR EQUILIBRIUM | AFFINITY | EQUILIBRIUM CONSTANT | REACTION ENTHALPY CHANGE | PATTERNS OF BEHAVIOR IN COMMON REACTING SYSTEMS

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REMINDER FROM LAST TIME

PHASE RULE OF REACTING SYSTEMS

If a system consists of a mixture of molecular types, the atoms may spontaneously redistribute themselves among the various molecules that are present. In a closed system this arrangement necessarily occurs without changing the total number of atoms of each element in the system. Such a rearrangement is commonly called a chemical reaction.

If a system consists of e elements, n components (some of which are molecules), then the number of independent, stoichiometric reactions will be:

GENERAL TREATMENT OF A UNIVARIANT CHEMICAL REACTION

Consider a closed system in which a chemical reaction takes place:

$$|\nu_A|A + |\nu_B|B = |\nu_C|C + |\nu_D|D$$

in which A and B species are the reactants, C and D species are the products, ν_i are the stoichiometric coefficients. The stoichiometric coefficients are positive integers or simple fractional numbers. The same chemical reaction can also be written as:

$$\nu_C C + \nu_D D + \nu_A A + \nu_B B = 0$$

In this equation the stoichiometric coefficients ν_i are algebraic; ν_C and ν_D are conventionally taken as positive, instead ν_A and ν_B are conventionally taken as negative. This convention indicates that ν_C moles of C and ν_D moles of D are formed, and $|\nu_A|$ moles of A have reacted with $|\nu_B|$ moles of B. To generalize:

$$\sum_i \nu_i M_i = 0 \qquad\qquad i = 1,2,\ldots,n$$

M_i refers to chemical species *i*, and *n* is the number of species present in the system. When **only one reaction** occurs in a **closed system** the variation of the number of moles of each species are not independent:

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_C}{\nu_C} = \frac{dn_D}{\nu_D} = \Delta\xi$$

CONDITIONS FOR EQUILIBRIUM | APPLICATION OF 1ST AND 2ND LAW

Consider a gas mixture containing the three components O_2, CO, and CO_2. This is a univariant system. Only one stoichiometric chemical reaction can be written:

To find the conditions for equilibrium, we write the combined statement of first and second laws for this multicomponent, single phase system:

THE CONSTRAINTS OF THE SYSTEM | CONSERVATION EQUATIONS

The system is isolated from its surroundings and the reaction is taking place at constant temperature and pressure:

We also know that isolated systems no matter crosses the boundaries…

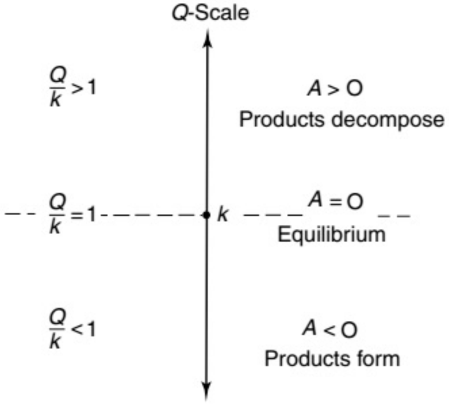
GIBBS FREE ENERGY IS AT A MINIMUM AT EQUILIBRIUM | AFFINITY

The system attains equilibrium when its composition arrives at the state for which the chemical potential of the reactants equals that of the products.

GIBBS FREE ENERGY | PROPER QUOTIENT & EQUILIBRIUM CONSTANT

Consider the general reaction: $|\nu_A|A + |\nu_B|B = |\nu_C|C + |\nu_D|D$

For which $A = \mu_{products} - \mu_{reactants}$



We know that the chemical potential is equal:

REACTION ENTHALPY CHANGE

Consider a system at the stationary state in which solid carbon and oxygen are made to react in order to form CO_2 at 298K and 1atm, as written in the following reaction:

$$\mathrm{C_{(s)} + O_2 = CO_2}$$

From the first law and since we are at 1atm and room temperature, this change of enthalpy is the standard enthalpy of reaction.

$$q = \Delta H^0 = H_{prod} - H_{react} = \sum \nu_i h_i^0 = \nu_{CO_2} h_{CO_2}^0 - \nu_C h_C^0 - \nu_{O_2} h_{O_2}^0$$

If we performed the experiment in the lab we would obtain $Q = -393.5\ \mathrm{KJ}$ (released from the system). Therefore:

$$\Delta H = \nu_{CO_2} h_{CO_2}^0 - \nu_C h_C^0 - \nu_{O_2} h_{O_2}^0 = -393.5\ \mathrm{KJ}$$

Since we know that $h_C = 0$ and $h_{O_2} = 0$ because Carbon and Oxygen are both in their reference states, **the specific enthalpy of formation of CO_2 at 298 K and 1 atm is -393.5 KJ/mol.** This leads to:

$$\Delta H = \Delta_f H_{CO_2}$$

REACTION ENTHALPY CHANGE | HESS'S LAW

Let's consider another example: The Oxidation of Methane at 298 K:

$$\mathrm{CH_4 + 2O_2 = CO_2 + 2H_2O}$$

Such reaction can be re-written as the sum of 3 reactions:

1. $\mathrm{C+O_2 = CO_2}$ $\Delta\mathrm{H} = \Delta_\mathrm{f}\mathrm{H}_{\mathrm{CO_2}}$
2. $\mathrm{2H_2+O_2 = 2H_2O}$ $\Delta\mathrm{H} = 2\Delta_\mathrm{f}\mathrm{H}_{\mathrm{H_2O}}$
3. $\mathrm{C+2H_2 = CH_4}$ $\Delta\mathrm{H} = \Delta_\mathrm{f}\mathrm{H}_{\mathrm{CH_4}}$

The enthalpy change for such chemical reaction can be written as:

$$\Delta_{reaction}H = \Delta_f H_{CO_2} + 2\Delta_f H_{H_2O} - \Delta_f H_{CH_4}$$

Therefore, at a specific temperature T, the reaction enthalpy change is:

$$\Delta_{reaction}H_T = \sum_{products} \nu_{prod}\,\Delta_f\, h_T - \sum_{reactants} \nu_r\,\Delta_f\, h_T$$

REACTION ENTHALPY CHANGE AT DIFFERENT TEMPERATURES

In order to compute the enthalpy change for a chemical reaction that happens at a temperature different from 298 K (standard temperature), the heat capacities at constant pressure, C_p's, are needed. (Kirchhoff's equations)

If $C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$ does not change with temperature:

$$H_T - H_{298} = \int_{298}^{T} C_p dT$$

If C_P does change with temperature, it can be expressed in a polynomial form such as $C_P = A + BT + CT^{-2} + DT^2$ and therefore:

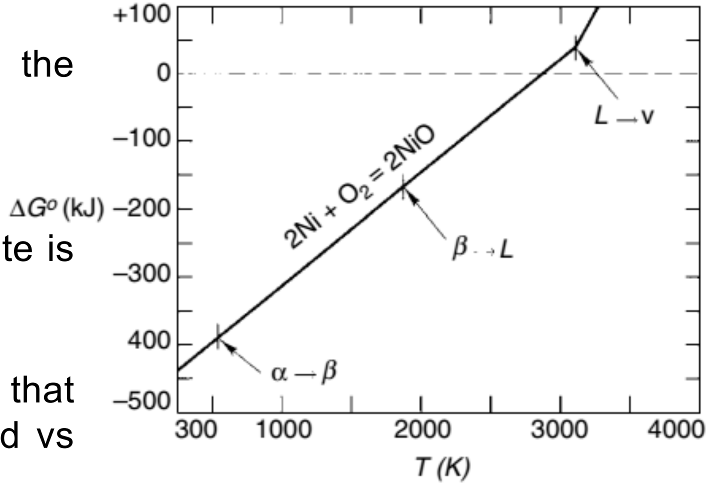
$$H_T - H_{298} = \int_{298}^{T} (A + BT + CT^{-2} + DT^2)\, dT$$

Since enthalpy is a state function the change of enthalpy for a reaction at a temperature different from 298K can be finally written as:

$$\Delta_{reaction} H_T = \Delta_{reaction} H_{298} + \int_{298}^{T} \left[\sum (\nu c_p)_{products} - \sum (\nu c_p)_{reactants} \right] dT$$

Patterns of Behavior in Common Reacting Systems | Richardson-Ellingham Charts for Oxidation

This is a plot of the formation energies of NiO. The curve has three discontinuities.
They are associated with phase changes of the components in the reaction.

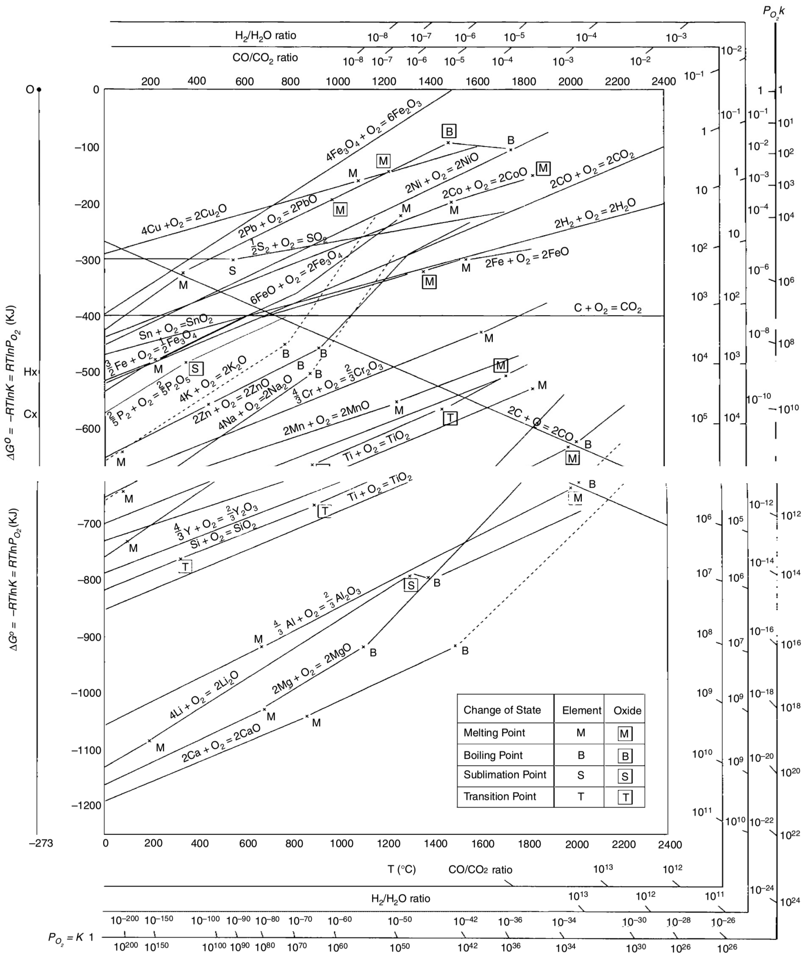


For example at 1450 ºC, Ni metal melts. Below that, the reference state is pure crystalline (fcc) nickel.

The enthalpies and entropies of these reactions differ by amounts that correspond to the difference in reference states for the nickel in liquid vs crystalline state.

The most drastic change of slope occurs at 3380 ºC is associated with the vaporization of Ni.

PATTERNS OF BEHAVIOR IN COMMON REACTING SYSTEMS | RICHARDSON-ELLINGHAM CHARTS FOR OXIDATION



Standard free energies changes for a range of oxidation reactions are plotted as a function of temperature. The curve representing each reaction is a broken line, with changes in slope occurring at phase changes for the metal or the oxide.

At low temperature where both metal and oxide are solid phases, the lines all have essentially the same slope | nearly identical standard entropy changes.

The major differences between the curves are contained in the heats of reaction. The order of the reaction lines from the top to the bottom of the chart is primary determined by the corresponding heat of reaction per mole of oxygen consumed.