Textbook: J. M. Smith, H. C. Van Ness, M.M. Abbott, **Introduction to Chemical Engineering Thermodynamics,** Seventh Edition, McGraw-Hill International Editions, 2005.

Supplementary References

Stanley I. Sandler, **Chemical and Engineering Thermodynamics,** Third edition John Wiley & Sons Inc, 1998.

J. Richard Elliott, Carl T. Lira, **Introductory Chemical Engineering Thermodynamics,** 2nd edition Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.

TOPICS IN PHASE EQUILIBRIUM

Consider a closed system containing an arbitrary number of species and comprised of an arbitrary number of phases in which the temperature and pressure are uniform (though not necessarily constant). The system is assumed to be initially in a nonequilibrium state with respect to mass transfer between phases and chemical reaction. Any changes which occur in the system are necessarily irreversible, and they take the system ever closer to an equilibrium state. We may imagine that the system is placed in surroundings such that the system and surroundings are always in thermal and mechanical equilibrium. Heat exchange and expansion work are then accomplished reversibly. Under these circumstances the entropy change of the surroundings is given by

$$dS_{surr} = \frac{dQ_{surr}}{T_{surr}} = -\frac{dQ}{T}$$

The final term applies to the system, for which the heat transfer dQ has a sign opposite to that of dQ_{surr}, and the temperature of the system T replaces T_{surr}, because both must have the same value for reversible heat transfer. The second law requires that

$$dS + dS_{surr} \geq 0$$

where S^t is the total entropy of the system. Combination of these expressions yields, upon rearrangement:

$$dQ \leq T\, dS^t$$

Application of the first law provides

$$dU^t = dQ + dW = dQ - P\, dV^t$$

$$dQ = dU^t + P\,dV^t$$

Combining this equation with Eq. gives

$$dU^t + P\,dV^t \le T\,dS^t$$

or

$$\boxed{dU^t + P\,dV^t - T\,dS^t \le 0}$$

Since this relation involves properties only, it must be satisfied for changes in state of *any* closed system of uniform T and P, without restriction to the conditions of mechanical and thermal reversibility assumed in its derivation. The inequality applies to every incremental change of the system between nonequilibrium states, and it dictates the direction of change that leads toward equilibrium. The equality holds for changes between equilibrium states (reversible processes).

or

$$d(U^t + PV^t - TS^t)_{T,\,P} \leq 0$$

From the definition of the Gibbs energy [Eq. (6.3)],

$$G^t = H^t - TS^t = U^t + PV^t - TS^t$$

Therefore

$$(dGt)T, P \leq 0$$

Equation) indicates that all irreversible processes occurring at constant T and P proceed in such a direction as to cause a decrease in the Gibbs energy of the system. Therefore:

The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P.

This criterion of equilibrium provides a general method for determination of equilibrium states. One writes an expression for G^t as a function of the numbers of moles (mole numbers) of the species in the several phases, and then finds the set of values for the mole numbers that minimizes G^t, subject to the constraints of mass conservation. This procedure can be applied to problems of phase, chemical-reaction, or combined phase and chemical-reaction equilibrium; it is most useful for complex equilibrium problems,

At the equilibrium state differential variations can occur in the system at constant T and P without producing any change in G^t. This is the meaning of the equality in Eq. Thus another form of this criterion of equilibrium is

$$(dG^t)_{T,P} = 0$$

Heat of Adsorption (Adsorpsiyon Isısı)

The Clapeyron equation, derived in Sec. 6.3 for the latent heat of phase transition of pure chemical species, is also applicable to pure-gas adsorption equilibrium. Here, however, the two-phase equilibrium pressure depends not only on temperature, but on surface coverage or the amount adsorbed. Thus the analogous equation for adsorption is written

$$\left(\frac{\partial P}{\partial T}\right)_n = \frac{\Delta H^{av}}{T \Delta V^{av}}$$

where subscript n signifies that the derivative is taken at constant amount adsorbed. Superscript av denotes a property change of *desorption*, i.e., the difference between the vapor-phase and the adsorbed-phase property. The quantity $\Delta H^{av} \equiv H^{v} - H^{a}$ is defined as the *isosteric heat of adsorption*, and is usually a positive quantity.[15] The heat of adsorption is a useful indication of the strength of the forces binding adsorbed molecules to the surface of the adsorbent, and its magnitude can therefore often be used to distinguish between physical adsorption and chemisorption.

The dependence of heats of adsorption on surface coverage has its basis in the energetic heterogeneity of most solid surfaces. The first sites on a surface to be occupied are those which attract adsorbate molecules most strongly and with the greatest release of energy. Thus the heat of adsorption decreases with surface coverage. Once all sites are occupied and multilayer adsorption begins, the dominant forces become those between adsorbate molecules, and for subcritical species the decreasing heat of adsorption approaches the heat of vaporization.

Assumed in the derivation of the Langmuir isotherm is the energetic equivalence of all adsorption sites, implying that the heat of adsorption is independent of surface coverage. This explains in part the inability of the Langmuir isotherm to provide a close fit to most experimental data over a wide range of surface coverage. The Freundlich isotherm, Eq. implies a logarithmic decrease in the heat of adsorption with surface coverage.

As in the development of the Clausius/Clapeyron equation if for low pressures one assumes that the gas phase is ideal and that the adsorbate is of negligible volume compared with the gas-phase volume, Eq. becomes

$$\left(\frac{\partial \ln P}{\partial T}\right)_n = \frac{\Delta H^{av}}{RT^2}$$

Application of this equation requires the measurement of isotherms,

For chemisorption, ΔH^{av} values usually range from 60 to 170 kJ mol^{-1}. For physical adsorption, they are smaller. For example, measured values at very low coverage for the physical adsorption of nitrogen and n-butane on 5A zeolite are 18.0 and 43.1 kJ mol^{-1}, respectively.