

**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.

# Effect of Temperature on the Equilibrium Constant

Since the standard-state temperature is that of the equilibrium mixture, the standard property changes of reaction, such as  $\Delta G^\circ$  and  $\Delta H^\circ$ , vary with **the equilibrium temperature**. The dependence of  $\Delta G^\circ$  on  $T$  is given by Eq. which may be rewritten as

$$\frac{d(\Delta G^\circ/RT)}{dT} = \frac{-\Delta H^\circ}{RT^2}$$

According to Eq.

$$\frac{\Delta G^\circ}{RT} = -\ln K$$

Therefore

$$\boxed{\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}}$$

$$\ln \frac{K}{K_1} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right)$$

**This approximate equation implies that a plot of  $\ln K$  vs. the reciprocal of absolute temperature is a straight line. Figure , a plot of  $\ln K$  vs.  $1/T$  for a number of common reactions, illustrates this near linearity. Thus, Eq. provides a reasonably accurate relation for the interpolation and extrapolation of equilibrium-constant data.**

**A convenient starting point for *rigorous* development of the effect of temperature on the equilibrium constant is the general relation**

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

**This equation follows from the definition of the Gibbs energy,  $G \equiv H - TS$ , applied to each species of a chemical reaction in its standard state at temperature  $T$ ; thus**

$$G_i^\circ = H_i^\circ - TS_i^\circ$$

**Multiplication by  $v_i$  and summation over all species gives**

$$\sum_i v_i G_i^\circ = \sum_i v_i H_i^\circ - T \sum_i v_i S_i^\circ$$

**The standard heat of reaction** is related to temperature by Eq. :

$$\Delta H^\circ = \Delta H_0^\circ + R \int_{T_0}^T \frac{\Delta C_P}{R} dT$$

The temperature dependence of the standard entropy change of reaction is developed similarly. **Equation** is written for **the standard-state entropy of species  $i$**  at the constant standard-state pressure  $P_o$ :

$$dS_i^\circ = C_{P_i}^\circ \frac{dT}{T}$$

**Multiplying by  $\nu_i$** , summing over all species, and invoking the definition of a standard property change of reaction transforms this equation into

$$dS^\circ = \Delta C_P^\circ \frac{dT}{T}$$

**Integration gives**

$$\Delta S^{\circ} = \Delta S_0^{\circ} + R \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} \frac{dT}{T}$$

**where  $\Delta S^{\circ}$  and  $\Delta S_0^{\circ}$  are standard entropy changes of reaction at temperature  $T$  and at reference temperature  $T_0$  respectively.**

$$\Delta G^{\circ} = \Delta H_0^{\circ} + R \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} dT - T \Delta S_0^{\circ} - RT \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} \frac{dT}{T}$$

**However**

$$\Delta S_0^{\circ} = \frac{\Delta H_0^{\circ} - \Delta G_0^{\circ}}{T_0}$$

whence

$$\Delta G^{\circ} = \Delta H_0^{\circ} - \frac{T}{T_0} (\Delta H_0^{\circ} - \Delta G_0^{\circ}) + R \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} dT - RT \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} \frac{dT}{T}$$

Finally, division by RT yields

$$\frac{\Delta G^{\circ}}{RT} = \frac{\Delta G_0^{\circ} - \Delta H_0^{\circ}}{RT_0} + \frac{\Delta H_0^{\circ}}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} dT - \int_{T_0}^T \frac{\Delta C_P^{\circ}}{R} \frac{dT}{T}$$

$$\ln K = -\Delta G^{\circ}/RT.$$

# Evaluation of Equilibrium Constants

Values of  $\Delta G^\circ$  for many *formation reactions* are tabulated in standard references.<sup>4</sup> The reported values of  $\Delta G_f^\circ$  are not measured experimentally

**The determination of  $\Delta S_f^\circ$**  may be based on the third law of thermodynamics, discussed before . Combination of values from Eq. for the absolute entropies of the species taking part in the reaction gives **the value of  $\Delta S_f^\circ$**  .

**Entropies (and heat capacities)** are also commonly determined from **statistical calculations based on spectroscopic data.**<sup>5</sup>

**We list values of  $\Delta G_{f_{298}}^\circ$**  for a limited number of chemical compounds **in Table C.4 of App. C.** These are for a temperature of 298.15 K, as are the values of  $\Delta H_{f_{298}}^\circ$  listed in the same table.

**Values of  $\Delta G^\circ$**  for other reactions are calculated from values for formation reactions in exactly **the same way that  $\Delta H^\circ$  values** for other reactions are determined from

# Relation of Equilibrium Constants to Composition

## Gas-Phase Reactions

The standard state for a gas is the ideal-gas state of the pure gas at the standard-state pressure  $P^0$  of 1 bar. Since the fugacity of an ideal gas is equal to its pressure,  $f_i^0 = P^0$  for each species  $i$ . Thus for gas-phase reactions  $\hat{a}_i = \hat{f}_i / f_i^0 = \hat{f}_i / P^0$ , and Eq. becomes

$$K = \prod_i \left( \frac{\hat{f}_i}{P^0} \right)^{v_i}$$

The equilibrium constant  $K$  is a function of temperature only. However, Eq. relates  $K$  to fugacities of the reacting species as they exist in the real equilibrium mixture. These fugacities reflect the nonidealities of the equilibrium mixture and are functions of temperature, pressure, and composition. This means that for a fixed temperature the composition at equilibrium must change with pressure in such a way that  $\prod_i (\hat{f}_i / P^0)^{v_i}$  remains constant.