

12.1: Effects of Temperature

For some of the derivations in this chapter, we will need an expression for the rate at which the ratio μ_i/T varies with temperature in a phase of fixed composition maintained at constant pressure. This expression leads, among other things, to an important relation between the temperature dependence of an equilibrium constant and the standard molar reaction enthalpy.

12.1.1 Variation of μ_i/T with temperature

In a phase containing species i , either pure or in a mixture, the partial derivative of μ_i/T with respect to T at constant p and a fixed amount of each species is given by

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{p, \{n_i\}} = \frac{1}{T} \left(\frac{\partial \mu_i}{\partial T} \right)_{p, \{n_i\}} - \frac{\mu_i}{T^2}$$

This equality comes from a purely mathematical operation; no thermodynamics is involved.

The relation is obtained from the formula $d(uv)/dx = u(dv/dx) + v(du/dx)$ (Appendix E), where u is $1/T$, v is μ_i , and x is T .

The partial derivative $(\partial \mu_i / \partial T)_{p, \{n_i\}}$ is equal to $-S_i$ (Eq. 9.2.48), so that Eq. 12.1.1 becomes

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{p, \{n_i\}} = -\frac{S_i}{T} - \frac{\mu_i}{T^2} = -\frac{TS_i + \mu_i}{T^2}$$

The further substitution $\mu_i = H_i - TS_i$ (Eq. 9.2.46) gives finally

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{p, \{n_i\}} = -\frac{H_i}{T^2}$$

For a pure substance in a closed system, Eq. 12.1.3 when multiplied by the amount n becomes

$$\left[\frac{\partial(G/T)}{\partial T} \right]_p = -\frac{H}{T^2}$$

This is the *Gibbs–Helmholtz equation*.

12.1.2 Variation of μ_i°/T with temperature

If we make the substitution $\mu_i = \mu_i^\circ + RT \ln a_i$ in Eq. 12.1.3 and rearrange, we obtain

$$\frac{d(\mu_i^\circ/T)}{dT} = -\frac{H_i}{T^2} - R \left(\frac{\partial \ln a_i}{\partial T} \right)_{p, \{n_i\}}$$

Because μ_i°/T is a function only of T , its derivative with respect to T is itself a function only of T . We can therefore use any convenient combination of pressure and composition in the expression on the right side of Eq. 12.1.5 in order to evaluate $d(\mu_i^\circ/T)/dT$ at a given temperature.

If species i is a constituent of a gas mixture, we take a constant pressure of the gas that is low enough for the gas to behave ideally.

the standard molar enthalpy H_i° (Eq. 9.3.7). In the expression for activity, $a_i(g) = \Gamma_i(g) \phi_i p_i/p$ (Table

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9.5), the pressure factor $\Gamma_i(g)$ is constant when p is constant, the fugacity coefficient ϕ_i for the ideal gas is unity, and $p_i/p = y_i$ is constant at constant $\{n_i\}$, so that the partial derivative $[\partial \ln a_i(g)/\partial T]_{p, \{n_i\}}$ is zero.

For component i of a condensed-phase mixture, we take a constant pressure equal to the standard pressure p° , and a mixture composition in the limit given by Eqs. 9.5.20–9.5.24 in which the activity coefficient is unity. H_i is then the standard molar enthalpy H_i° , and the activity is given by an expression in Table 9.5 with the pressure factor and activity coefficient set equal to 1: $a_i = x_i$, $a_A = x_A$, $a_{x,B} = x_B$, $a_{c,B} = c_B/c^\circ$, or $a_{m,B} = m_B/m^\circ$. With the exception of $a_{c,B}$, these activities are constant as T changes at constant p and $\{n_i\}$.

If solute B is an electrolyte, $a_{m,B}$ is given instead by Eq. 10.3.10; like $a_{m,B}$ for a nonelectrolyte, it is constant as T changes at constant p and $\{n_i\}$.

Thus for a gas-phase species, or a species with a standard state based on mole fraction or molality, $[\partial \ln a_i(g)/\partial T]_{p, \{n_i\}}$ is zero and Eq. 12.1.5 becomes

$$\frac{d(\mu_i^\circ/T)}{dT} = -\frac{H_i^\circ}{T^2}$$

Equation 12.1.6, as the conditions of validity indicate, does not apply to a solute standard state based on concentration, except as an approximation. The reason is the volume change that accompanies an isobaric temperature change. We can treat this case by considering the following behavior of $\ln(c_B/c^\circ)$:

$$\begin{aligned} \left[\frac{\partial \ln(c_B/c^\circ)}{\partial T} \right]_{p, \{n_i\}} &= \frac{1}{c_B} \left(\frac{\partial c_B}{\partial T} \right)_{p, \{n_i\}} = \frac{1}{n_B/V} \left[\frac{\partial (n_B/V)}{\partial T} \right]_{p, \{n_i\}} \\ &= V \left[\frac{\partial (1/V)}{\partial T} \right]_{p, \{n_i\}} = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p, \{n_i\}} \\ &= -\alpha \end{aligned}$$

Here α is the cubic expansion coefficient of the solution (Eq. 7.1.1). If the activity coefficient is to be unity, the solution must be an ideal-dilute solution, and α is then α_A^* , the cubic expansion coefficient of the pure solvent. Eq. 12.1.5 for a nonelectrolyte becomes

$$\frac{d(\mu_{c,B}^\circ/T)}{dT} = -\frac{H_B^\circ}{T^2} + R\alpha_A^*$$

12.1.3 Variation of $\ln K$ with temperature

The thermodynamic equilibrium constant K , for a given reaction equation and a given choice of reactant and product standard states, is a function of T and *only* of T . By equating two expressions for the standard molar reaction Gibbs energy, $\Delta_r G^\circ = \sum \nu_i \mu_i^\circ$ and $\Delta_r G^\circ = -RT \ln K$ (Eqs. 11.8.3 and 11.8.10), we obtain

$$\ln K = -\frac{1}{RT} \sum_i \nu_i \mu_i^\circ$$

The rate at which $\ln K$ varies with T is then given by

$$\frac{d \ln K}{dT} = -\frac{1}{R} \sum_i \nu_i \frac{d(\mu_i^\circ/T)}{dT}$$

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Combining Eq. 12.1.10 with Eqs. 12.1.6 or 12.1.8, and recognizing that $\sum_i \nu_i H_i^\circ$ is the standard molar reaction enthalpy $\Delta_r H^\circ$, we obtain the final expression for the temperature dependence of $\ln K$:

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2} - \alpha_A^* \sum_{\substack{\text{solute,} \\ \text{conc. basis}}} \nu_i$$

The sum on the right side includes only solute species whose standard states are based on concentration. The expression is simpler if all solute standard states are based on mole fraction or molality:

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

We can rearrange Eq. 12.1.12 to

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

We can convert this expression for $\Delta_r H^\circ$ to an equivalent form by using the mathematical identity $d(1/T) = -(1/T^2)dT$:

$$\Delta_r H^\circ = -R \frac{d \ln K}{d(1/T)}$$

Equations 12.1.13 and 12.1.14 are two forms of the **van't Hoff equation**. They allow us to evaluate the standard molar reaction enthalpy of a reaction by a noncalorimetric method from the temperature dependence of $\ln K$. For example, we can plot $\ln K$ versus $1/T$; then according to Eq. 12.1.14, the slope of the curve at any value of $1/T$ is equal to $-\Delta_r H^\circ / R$ at the corresponding temperature T .

A simple way to derive the equation for this last procedure is to substitute $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ in $\Delta_r G^\circ = -RT \ln K$ and rearrange to

$$\ln K = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta_r S^\circ}{R}$$

Suppose we plot $\ln K$ versus $1/T$. In a small temperature interval in which $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are practically constant, the curve will appear linear. According to Eq. 12.1.15, the curve in this interval has a slope of $-\Delta_r H^\circ / R$, and the tangent to a point on the curve has its intercept at $1/T = 0$ equal to $\Delta_r S^\circ / R$.

When we apply Eq. 12.1.14 to the *vaporization process* $A(l) \rightarrow A(g)$ of pure A, it resembles the Clausius–Clapeyron equation for the same process (Eq. 8.4.15). These equations are not exactly equivalent, however, as the comparison in Table 12.1 shows.

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