Chapter 10

The Third Law of Thermodynamics

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10.1 Statement of the Third Law

- The third law of thermodynamics is concerned with the behavior of systems in equilibrium as their temperature approaches zero

- The definition of entropy given by

$$S = \int_0^T \frac{dQ_r}{T} + S_0 \tag{10.1}$$

Is incomplete because of the undetermined additive constant S_0, the entropy at absolute zero.

- In this chapter we shall introduce a principle that will enable us to determine S_0.

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- Gibbs-Helmholtz equation

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \qquad (10.2)$$

- If this relation is applied to the initial and final states of a system undergoing an isothermal process, it takes the form

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \qquad (10.3)$$

- This shows that the change in enthalpy and the change in the Gibbs function are equal at T = 0 for an isobaric process.

$$\lim_{T\to 0}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = 0 \qquad \lim_{T\to 0}\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = 0 \qquad (10.4)$$

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- Equation (10.4) is illustrated in Figure 10.1.

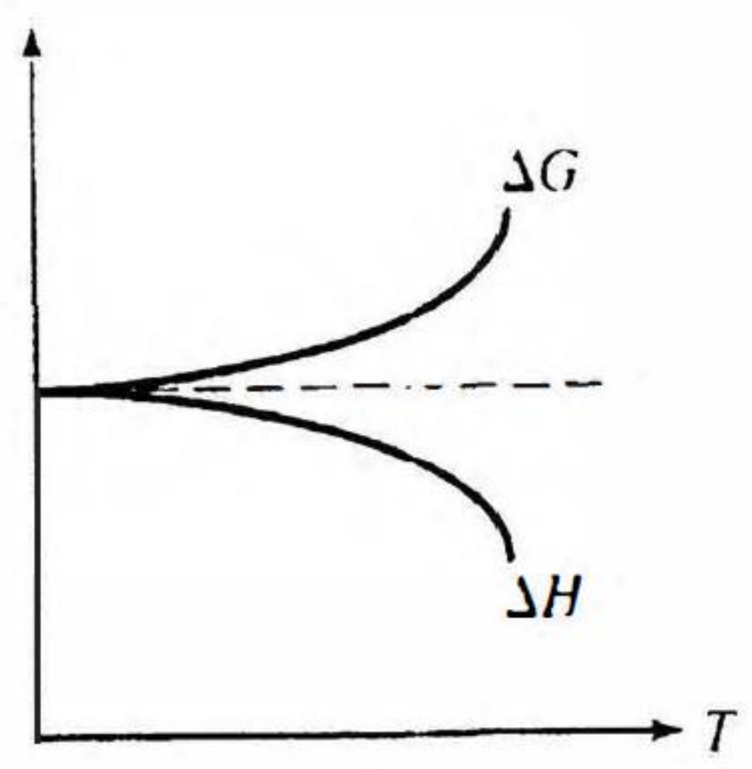

Figure 10.1 Variation of ΔG and ΔH in the vicinity of absolute zero.

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- We may write the equation (10.4) as

$$\lim_{T\to 0}\left[\frac{\partial(G_2-G_1)}{\partial T}\right]_P = \lim_{T\to 0}\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right] = 0 \qquad (10.5)$$

where the subscripts 1 and 2 refer to the initial and final states, respectively.

- From the reciprocity relation, we have **the Nernst formulation of the third law**.

$$\lim_{T\to 0}(S_1 - S_2) = 0 \qquad (10.6)$$

All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero.

$$^{*}\; G = U - TS + PV \;\rightarrow\; dG = -SdT + VdP \;\rightarrow\; S = -\left(\frac{\partial G}{\partial T}\right)_P$$

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- Planck extended Nernst's hypothesis by assuming that it holds for G_1 and G_2 separately.

$$\lim_{T\to 0} G(T) = \lim_{T\to 0} H(T) \qquad (10.7)$$

$$\lim_{T\to 0} \left(\frac{\partial G}{\partial T}\right)_P = \lim_{T\to 0} \left(\frac{\partial H}{\partial T}\right)_P \qquad (10.8)$$

- For convenience, we temporarily introduce a variable $\Phi \equiv G - H$. Equation (10.2) then becomes

$$T\left(\frac{\partial G}{\partial T}\right)_P - \Phi = 0 \qquad (10.9)$$

- Adding the term $-T(\partial H/\partial T)_P$ to both sides of Equation (10.9), we get

$$\mathrm{T}\left(\frac{\partial \Phi}{\partial \mathrm{T}}\right)_{\mathrm{P}} - \Phi = -\mathrm{T}\left(\frac{\partial \mathrm{H}}{\partial \mathrm{T}}\right)_{\mathrm{P}} \qquad (10.10)$$

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- By L'Hopital's rule,

$$\lim_{T\to 0}\left(\frac{\partial H}{\partial T}\right)_P = 0 \qquad (10.11)$$

- Finally, by Equation (10.8), we obtain the result

$$\lim_{T\to 0}\left(\frac{\partial G}{\partial T}\right)_P = 0 \qquad (10.12)$$

- Since $\left(\frac{\partial G}{\partial T}\right)_P = -S$, it follows **the Planck's statement of the third law**.

$$\lim_{T\to 0} S = 0 \qquad (10.13)$$

The entropy of a true equilibrium state of a system at absolute zero is zero