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Reading Assignment 5

5.12 Using the Fact that S is a State Function to Determine the Dependence of S on V and T.

$\left(\frac{\partial S}{\partial T}\right)_V$, derived from $dS = \frac{dU}{T} + \frac{P}{T}dV$

$$dS = \boxed{\frac{C_V}{T}}\,dT + \boxed{\frac{\beta}{\kappa}}\,dV$$

volume dependence

entropy differential (related to how entropy changes)

$\left(\frac{\partial S}{\partial V}\right)_T$, eventually because $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{-(\partial V/\partial T)_P}{(\partial V/\partial P)_T}$

temperature dependence

5.13 The Dependence of S on T and P

$\left(\frac{\partial S}{\partial T}\right)_P$, derived from $dS = \frac{dH}{T} - \frac{V}{T}dP$

$$dS = \boxed{\frac{C_P}{T}}\,dT - \boxed{V\beta}\,dP$$

pressure dependence

entropy differential

$\left(\frac{\partial S}{\partial P}\right)_T$, eventually because $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\beta$

temperature dependence

6.1 The Gibbs Energy and the Helmholtz Energy

$\boxed{A \equiv U - TS}$ → Helmholtz Energy, describes an <u>isochoric</u> spontaneous process if $\Delta A \leq 0$

$\boxed{G \equiv H - TS}$ → Gibbs Energy, describes an <u>isobaric</u> spontaneous process if $\Delta G \leq 0$

6.2 The Differential Forms of U, H, A, and G

$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V$

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

<u>Differentials</u> (Derived from definitions of H, A, and G)

$dU = TdS - PdV$

$dH = TdS + VdP$

$dA = -SdT - PdV$

$dG = -SdT + VdP$

Maxwell Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} \qquad -\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P = V\beta$$

6.3 The Dependence of the Gibbs and Helmholtz Energies on P, V, and T

Dependences

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad (<0) \qquad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad (<0)$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (<0) \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \quad (>0)$$

Increasing temperature and volume makes processes more spontaneous while increasing pressure makes processes less spontaneous.

Finding Gibbs Energy:

$$G(T,P) = G^\circ(T,P^\circ) + \int_{P^\circ}^{P} V\,dP'$$

Gibbs energy at a given temperature and pressure

Gibbs energy at a reference pressure

Perturbation in Gibbs energy due to change in pressure