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Reading Assignment 6

5.12: Using the fact that S is a state function to determine the dependence of S on V and T

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

- B/c, 1/T, and P/T are greater than zero, the etropy of a system increases with the internal energy at constant volume + increases with the volume at constant internal energy.

- We first write the total differential dS in terms of the partial derivatives with respect to V + T

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

- To evaluate $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$ for dS:

$$dS = \frac{1}{T}\left[C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right] + \frac{P}{T}dV = \frac{C_V}{T}dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]dV$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

- The expressions for $(\partial S/\partial V)_T$ is not a form that allows for a direct comparison with experiment to be made

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T$$

- Taking the mixed second derivative

$$\left(\frac{\partial}{\partial V}\right)\left(\frac{\partial S}{\partial T}\right)_V\Big)_T = \frac{1}{T}\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T}\left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right] - \frac{1}{T^2}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

Simplify

$$P + \left(\frac{\partial U}{\partial V}\right)_T = T\cdot\left(\frac{\partial P}{\partial T}\right)_V$$

A practical equation is obtained for the dependance of entropy on volume under constant temp conditions:

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

The result of these considerations is that dS can be expressed in terms of dT and dV as:

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

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV$$

5.13: The dependence of S on T and P

The total differential ds is written in the form

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

- starting from the relation $U = H - PV$ total differential dU:

$$dU = TdS - PdV = dH - PdV - VdP$$

$$dS = \frac{1}{T} dH - \frac{V}{T} dP$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dS = \frac{C_P}{T} dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

The coefficiant of dT and dP must be same on both sides:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \text{and} \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

Just as in our evaluation of $(\partial S/\partial V)_T$ we equate the mixed second partial derivatives of $(\partial S/\partial T)_P$ and $(\partial S/\partial P)_T$:

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

There mixed partial derivative can be evaluated

$$\left(\frac{\partial}{\partial P}\right)\left(\left(\frac{\partial S}{\partial T}\right)_P\right)_T = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right)_T$$

$$\left(\frac{\partial}{\partial T}\right)\left(\left(\frac{\partial S}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\right] - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right.$$

$$\frac{1}{T}\left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right)_P = \frac{1}{T}\left[\left(\frac{\partial}{\partial T}\left(\frac{\partial}{\partial T}\right)\left(\frac{\partial H}{\partial P}\right)_T\right)_P - \left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{T^2}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right.\right.$$

Simplify

$$\left(\frac{\partial H}{\partial P}\right)_T - V = -T\left(\frac{\partial V}{\partial T}\right)_P$$

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

Using these results, the total differential ds can be written in terms of experimentally accessible parameter as:

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

integrating both sides:

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

6.1 The Gibbs Energy and the Helmholtz Energy

The fundamental expression governing spontaneity is the Clausius inequality, written in the form.

$$TdS \geq đq$$

The quality is satisfied only for a reversible process B/c $đq = dU - đw$

$$TdS \geq dU - đw \text{ , or } -dU + đw + TdS \geq 0$$

It's useful to distinguish between expansion work, in which work arises from a volume change in system nonexpansion work

$$-dU - P_{external} dV + đw_{nonexpansion} + TdS \geq 0$$

For isothermal processes, $TdS = d(TS)$

$$-dU + TdS \geq - đw_{expansion} - đw_{nonexpansion} \text{ or}$$

$$d(U - TS) \leq đw_{expansion} + đw_{nonexpansion}$$

The combination of state function $U - TS$, which has the units of energy, defines a new state function that we call the Helmholtz energy, abbreviated A.

$$dA = đw_{expansion} - đw_{nonexpansion} \leq 0$$

$$đw_{total} = đw_{expansion} + đw_{nonexpansion} \geq dA$$

If nonexpansion work also is not possible in the tranformation $đw_{nonexpansion} = đw_{expansion} = 0$ the condition that defines spontaneity and equilibrium becomes

$$dA \leq 0$$

using the relation $H = U + PV$

$$d(U + PV - TS) = d(H - TS) \leq đw_{nonexpansion}$$

The combination of state functions $H - TS$, which has the units of energy, defines a new state function called the Gibbs energy, G

$$dG - đw_{nonexpansion} \leq 0$$

$$dG \leq 0$$

Clausius inequality

$$dS - \frac{đq}{T} \geq 0$$

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

Maximum nonexpansion work: can be produced by a chemical transformations
For macroscopic changes at constant P and T in which no nonexpansion work is possible, the condition for spontaneity is $\Delta G_R < 0$ where:

$$\Delta G_R = \Delta H_R - T\Delta S_R$$

- The entropic contribution to ΔG_R is greater for higher temp
- The chemical transformation is always spontaneous if $\Delta H_R < 0$ + $\Delta S_R > 0$
- The chemical transformation is always nonspontaneous if $\Delta H_R > 0$ + $\Delta S_R < 0$
- The relative magnitudes of ΔH_R + $T\Delta S_R$, determine if chemical trans. is spontaneous
- If the chemical reaction is not spontaneous, then the reverse process is spontaneous
- If $\Delta G_R = 0$, the reaction mixture is at equilibrium, + neither direction of Δ is spontaneous
- For macroscopic changes at constant V+T in which no nonexpansion work is possible, the condition for sponteity is $\Delta A_R < 0$ where

$$\Delta A_R = \Delta U_R - T\Delta S_R$$

6.2: The differential forms of U, H, A, and G

- Differential forms are essential in calculating how U, H, A, G vary with state variable such as P and T. Starting from the definitions:

$$H = U + PV$$
$$A = U - TS$$
$$G = H - TS = U + PV - TS$$

The following total differentials can be formed:

$$dU = TdS - PdV$$
$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$
$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$
$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

Although other combinations variables can be used, these natural variables are used b/c the differential expression are compact

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

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

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

These expressions states how U, H, A and G vary with their natural variables