Statistical Molecular Thermodynamics

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Video 7.1

Entropy and Other Thermodynamic Functions

Manipulating Differentials

1st Law + 2nd Law

$$\delta q_{rev} = TdS$$

$$dU = \delta w_{rev} + \delta q_{rev},$$

$$\delta w_{rev} = -PdV$$

$$dU = TdS - PdV$$

Now, consider the total differential of U with respect to T and V

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

$\left(\frac{\partial U}{\partial T}\right)_V = C_V(T)$

We can equate these two expressions for dU and solve for dS

Solution for dS

$$TdS - PdV = C_V(T)dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Which rearranges to:

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

= 0 for ideal gas

Considering the total differential of S with respect to T and V

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

We have,

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

The Differential of Enthalpy

$$dU = TdS - PdV$$

$$dH = d(U + PV)$$
$$= dU + VdP + PdV$$
$$= TdS - PdV + VdP + PdV = TdS + VdP$$

Now, consider the total differential of H with respect to T and P

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

$C_P(T)$ → $\left(\frac{\partial H}{\partial T}\right)_P$

We can equate these two expressions for dH and solve for dS

Solution for dS

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

Which rearranges to:

= 0 for ideal gas

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

Considering the total differential of S with respect to T and P

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

We have,

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

Absolute Entropy Values

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

integrate with respect to T at constant P to determine entropy change with temperature change

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_P(T)dT}{T}$$

Let $T_1 = 0\ \mathrm{K}$

$$S(T_2) = S(0) + \int_0^{T_2} \frac{C_P(T)dT}{T}$$

Thus, we can calculate the entropy of a substance at *any temperature* T_2 if we know the entropy at 0 K and the constant pressure heat capacity