Statistical Molecular Thermodynamics

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Video 7.1

Entropy and Other Thermodynamic Functions
Manipulating Differentials

\[ dU = \delta w_{rev} + \delta q_{rev} \]

- \( PdV \)

\[ \delta q_{rev} = TdS \]

1\(^{\text{st}}\) Law + 2\(^{\text{nd}}\) Law

\[ dU = TdS - PdV \]

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

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

\( C_V(T) \)

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:

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

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,

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

= 0 for ideal gas
The Differential of Enthalpy

\[ dH = d(U + PV) \]
\[ = dU + VdP + PdV \]
\[ = TdS - PdV + VdP + PdV = TdS + VdP \]

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

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

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

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:

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

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,

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

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

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

Let \( T_1 = 0 \) K

\[ S(T_2) = S(0) + \int_{0}^{T_2} \frac{C_P(T)}{T} dT \]

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.