Statistical Molecular Thermodynamics

Christopher J. Cramer

Video 8.6

Natural Independent Variables
Working with the Simplest Forms

\[ dU = TdS - PdV \]  (first and second laws)

If we consider \( S \) and \( V \) as independent variables of \( U \), the coefficients of \( dS \) and \( dV \) are \textit{simple} thermodynamic functions.

\[
dU = \left( \frac{\partial U}{\partial S} \right)_V dS + \left( \frac{\partial U}{\partial V} \right)_S dV \quad \rightarrow \quad \left( \frac{\partial U}{\partial S} \right)_V = T \quad \left( \frac{\partial U}{\partial V} \right)_S = -P
\]

Compare with, say, \( V \) and \( T \) as independent variables:

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

\[
= \left[ T\left( \frac{\partial P}{\partial T} \right)_V - P \right] dV + C_V dT
\]

see Video 8.3

considerably more complex

We thus refer to \( S \) and \( V \) as the \textit{natural independent variables} of \( U \)
Differentials to Date

Start from the first and second laws: 
\[ dU = TdS - PdV \]

Add \( d(PV) \) to both sides: 
\[ d(U + PV) = TdS - PdV + VdP + PdV \]

Subtract \( d(TS) \) from both sides: 
\[ d(U - TS) = TdS - PdV - TdS - SdT \]

Add \( d(PV) \) and subtract \( d(TS) \) from both sides: 
\[ d(U + PV - TS) = TdS - PdV + VdP + PdV - TdS - SdT \]

(All from the 1\(^{st}\) and 2\(^{nd}\) laws and definitions of \(H, A,\) and \(G\))
## Natural Independent Variables

<table>
<thead>
<tr>
<th>Function</th>
<th>Differential</th>
<th>Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>$dU = TdS - PdV$</td>
<td>$S$ and $V$</td>
</tr>
<tr>
<td>$S$</td>
<td>$dS = \frac{1}{T} dU + \frac{P}{T} dV$</td>
<td>$U$ and $V$</td>
</tr>
<tr>
<td>$H$</td>
<td>$dH = TdS + VdP$</td>
<td>$S$ and $P$</td>
</tr>
<tr>
<td>$A$</td>
<td>$dA = -SdT - PdV$</td>
<td>$T$ and $V$</td>
</tr>
<tr>
<td>$G$</td>
<td>$dG = -SdT + VdP$</td>
<td>$T$ and $P$</td>
</tr>
</tbody>
</table>
## Associated Maxwell Relations

<table>
<thead>
<tr>
<th>Function</th>
<th>Differential</th>
<th>Maxwell relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U$</td>
<td>$dU = TdS - PdV$</td>
<td>$(\frac{\partial T}{\partial V})_S = -\left(\frac{\partial P}{\partial S}\right)_V$</td>
</tr>
<tr>
<td>$H$</td>
<td>$dH = TdS + VdP$</td>
<td>$(\frac{\partial T}{\partial P})_S = \left(\frac{\partial V}{\partial S}\right)_P$</td>
</tr>
<tr>
<td>$A$</td>
<td>$dA = -SdT - PdV$</td>
<td>$(\frac{\partial S}{\partial V})_T = \left(\frac{\partial P}{\partial T}\right)_V$</td>
</tr>
<tr>
<td>$G$</td>
<td>$dG = -SdT + VdP$</td>
<td>$(\frac{\partial S}{\partial P})_T = -\left(\frac{\partial V}{\partial T}\right)_P$</td>
</tr>
</tbody>
</table>