Statistical Molecular Thermodynamics

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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 *simple* thermodynamic functions.

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \Rightarrow \quad \left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

Compare with, say, V and T as independent variables:

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

see Video 8.3

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

considerably more complex

We thus refer to S and V as the *natural independent variables* of U

Differentials to Date

Start from the first and second laws: $dU = TdS - PdV$

Add $d(PV)$ to both sides: $\longrightarrow$ $dH = TdS + VdP$

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

Subtract $d(TS)$ from both sides: $\longrightarrow$ $dA = -SdT - PdV$

$d(U-TS) = TdS-PdV-TdS-SdT$

Add $d(PV)$ and subtract $d(TS)$ from both sides: $\longrightarrow$ $dG = -SdT + VdP$

$d(U+PV-TS) = TdS-PdV+VdP+PdV-TdS-SdT$

(All from the 1st and 2nd laws and definitions of *H*, *A*, and *G*)

Natural Independent Variables

Function	Differential		Variables
U	$dU = TdS - PdV$	$\longrightarrow$	S and V
S	$dS = \frac{1}{T}dU + \frac{P}{T}dV$	$\longrightarrow$	U and V
H	$dH = TdS + VdP$	$\longrightarrow$	S and P
A	$dA = -SdT - PdV$	$\longrightarrow$	T and V
G	$dG = -SdT + VdP$	$\longrightarrow$	T and P

Associated Maxwell Relations

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