CHEM 331
Physical Chemistry
Revision 1.0

Thermodynamic State Functions

Internal Energy

U(S,V)* dU $= \left(\frac{\partial U}{\partial S}\right)_T dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

$= T\,dS - P\,dV$

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

$= C_v\,dT + \Pi_T\,dV$

Enthalpy

H(S,P)* dH $= \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$

$= T\,dS + V\,dP$

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

$= C_p\,dT - C_p\mu\,dP$

Entropy

S(U,V)* dS $= \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$

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

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

$= \frac{C_v}{T}\,dT + \frac{\alpha}{\kappa}\,dV$

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

$$= \frac{C_p}{T} dT - V\alpha\, dP$$

Helmholtz Free Energy

$$A(T,V)^* \qquad dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$= -S\, dT - P\, dV$$

Gibb's Free Energy

$$G(T,P)^* \qquad dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$= -S\, dT + V\, dP$$

*Fundamental thermodynamic relationships. According to Bromberg:

> In mechanics a conservative field is one for which a force is derivable from a potential. An analogous situation exists in thermodynamics in which an intensive property is obtained from the various thermodynamic functions, thus $P = -(\partial U/\partial V)_S$. Work terms arise from the product of an intensive property with its associated extensive property, for example, PdV. When we compare these work terms with the definition of work, Fdx, the intensive properties such as P take the form of generalized forces. For this reason, the functions U, H, A, and G are often referred to as *potentials*. Heat is also measured by the product of an intensive and an extensive property; in the expression TdS, the term T is the intensive and S the extensive property.
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> ... the four potentials [U, H, A, G] are written in terms of their natural variables [* relationships]. The energy U is a function of the *extensive* properties of the system, S and V. What we have accomplished in constructing H, A, and G from U is to substitute an intensive property for its associated extensive property. Enthalpy is generated from energy by replacing the extensive property V by its associated intensive property P. The Helmholtz energy A is generated by replacing S by T; and G is generated by simultaneously replacing S and V by T and P. These can be regarded as analogous to coordinate transformations such as the transformation from cartesian to polar coordinates. Here the transformation involves replacing an extensive property by its associated intensive property. When viewed in this light, the functions H, A, and G are simply the energy transformed into a different set of variables. In mathematics, such a transformation is known as a *Legendre transformation*.