

## 6.1 The Gibbs Energy and the Helmholtz Energy

- Gibbs and Helmholtz allows for spontaneity and equilibrium to be defined using only properties of the system rather than of the system and surroundings.
- remember Clausius inequality:  $TdS \geq dq$
- Helmholtz energy:  $dA = \delta w_{\text{expansion}} - \delta w_{\text{non-expansion}} \leq 0$
- Gibbs energy:  $dG = \delta w_{\text{non-expansion}} \leq 0$
- maximum non-expansion work
- $\Delta G_R = \Delta H_R - T\Delta S_R$
- $\Delta A_R = \Delta U_R - T\Delta S_R$        $\Delta A_R < 0$

## 6.2 The Differential Forms of $U, H, A$ and $G$

- $U, H$  used to calculate changes in energy for processes
- $A, G$  used to calculate direction in which processes evolve and the max work the reaction can produce.

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

internal energy as  $U(S, V)$

enthalpy as  $H(S, P)$

Helmholtz energy as  $A(T, V)$

Gibbs energy as  $G(T, P)$

natural  
variables

$$\left(\frac{\partial U}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$