

- the combination of state functions $U-TS$ which has units of energy defines a new state function Helmholtz energy
- general def. of general spontaneity for isothermal processes

$$\Delta A = \Delta w_{\text{expansion}} - \Delta w_{\text{nonexpansion}} \quad (6)$$

- way to calculate (6) @ max. work that a system can do on the surroundings in a isothermal process

$$\Delta w_{\text{total}} = \Delta w_{\text{expansion}} + \Delta w_{\text{nonexpansion}} \quad (7)$$

- constant volume process $dV=0$ which implies $\Delta w_{\text{exp}}=0$ because $dV=0$

- if non expansion $\rightarrow \Delta w_{\text{exp}} = \Delta w_{\text{expansion}} = 0$
- spontaneity and equilibrium

$$\Delta A \leq 0$$

- @ constant P and T , $PdV = d(PV)$ and $TdS = d(TS)$
- using $H = U + PV$

- combination of $H-TS$ defines a new state function: Gibbs energy (8)
- using Gibbs, the condition for spontaneity and equilibrium becomes:

- for isothermal process @ constant pressure

$$\Delta G - \Delta w_{\text{nonexpansion}} \leq 0 \quad (9)$$

- consider a transformation at constant P and T for which nonexpansion work is not possible
- equation (9) becomes

$$\Delta G \leq 0 \quad (10)$$

- Clausius inequality

$$dS - \frac{\delta q}{T} \geq 0 \quad (12)$$

- Clausius + $dS_{\text{surr}} = -\delta q/T$

$$dS + dS_{\text{surr}} \geq 0 \quad (13)$$

- $\rightarrow G$ and A are expressed only in terms of the macroscopic state variables of the system
- \rightarrow no longer nec. to consider the surr explic.
- $\rightarrow \Delta G$ and ΔA for the system alone is sufficient