

Physical Chemistry

Lecture 16
Free Energies

Spontaneity under arbitrary conditions

- ◆ At constant U and V, the criterion for spontaneity is $(\Delta S)_{U,V} \geq 0$
- ◆ Not a convenient set of conditions
- ◆ Often find constraints such as constant P and T, or constant T and V
- ◆ Consider idea from physics: minimization of energy

Free-energy functions

- ◆ Specify energy and entropy considerations in a system
- ◆ Helmholtz free energy, A, of a state
 $A = U - TS$
- ◆ Gibbs free energy, G, of a state
 $G = H - TS = U + PV - TS$
- ◆ Account for energy minimization and entropy maximization simultaneously

Differential Helmholtz free energy and spontaneity

- ◆ By definition
$$\begin{aligned}dA &= dU - TdS - SdT \\ &= dq + dw - TdS - SdT \\ &= (dq - TdS) - P_{ext}dV - SdT\end{aligned}$$
- ◆ Under constant-V, constant-T conditions
$$dA = (dq - TdS)$$
- ◆ For spontaneity under these conditions, this must be negative
$$(dA)_{T,V} \leq 0$$

Differential Gibbs free energy and spontaneity

- ◆ By definition
$$\begin{aligned}dG &= dH - TdS - SdT \\ &= dU + PdV + VdP - TdS - SdT \\ &= (dq - TdS) - (P_{ext} - P)dV + VdP - SdT\end{aligned}$$
- ◆ Under constant-P, constant-T conditions
$$dG = (dq - TdS)$$
- ◆ For spontaneity under these conditions, this must be negative
$$(dG)_{T,P} \leq 0$$

Free-energy criteria for spontaneity in an isolated system

- ◆ At constant V and T
$$(dA)_{T,V} \leq 0$$
- ◆ At constant P and T
$$(dG)_{T,P} \leq 0$$
- ◆ Like minimizing excess energy in a physical system

Helmholtz free energy in reversible processes

- ◆ Helmholtz free energy in a process

$$dA = (dq - TdS) + dw - SdT$$

- ◆ At constant T

$$dA = (dq - TdS) + dw$$

- ◆ Under reversible conditions, $dq = TdS$

$$dA = dw_{\max}$$

- ◆ The Helmholtz free-energy change represents the maximum work in the process

Gibbs free energy in reversible processes

- ◆ Gibbs free-energy change

$$dG = (dq - TdS) + dw + PdV + VdP - SdT$$

- ◆ At constant T and P

$$dG = (dq - TdS) + dw + PdV$$

- ◆ Under reversible conditions, $dq = TdS$ and $-PdV = -dw_{\max, \text{mech}}$

$$dG = dw - dw_{\max, \text{mech}}$$

- ◆ The Gibbs free-energy change represents the work in excess of the reversible mechanical work of a process

Differentials of free-energy functions

- ◆ Helmholtz free-energy change

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= TdS - PdV - TdS - SdT \\ &= -SdT - PdV \end{aligned}$$

- ◆ Gibbs free-energy change

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + VdP - TdS - SdT \\ &= -SdT + VdP \end{aligned}$$

Maxwell relations from the free-energy functions

- ◆ Cross partial derivatives of state functions are equal

- ◆ Helmholtz free energy

$$dA = -SdT - PdV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

- ◆ Gibbs free energy

$$dG = -SdT + VdP \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

- ◆ Useful for evaluating derivatives of entropy

Other forms of work

- ◆ Stretching an elastic network

$$dw_{\text{elastic}} = fdl$$

- ◆ Moving charge against an electric potential

$$dw_{\text{electric}} = Vdq$$

- ◆ Magnetizing a material

$$dw_{\text{magnetic}} = BdM$$

- ◆ Creating a surface

$$dw_{\text{surface}} = \gamma dA$$

Summary

- ◆ Spontaneity under specific conditions demands certain changes in state functions
- ◆ Free-energy functions specify spontaneity under common conditions
 - $(dA)_{T,V} \leq 0$
 - $(dG)_{T,P} \leq 0$
- ◆ Related to work
 - ΔA is maximum work in a process
 - ΔG is excess work (above maximum) in a process
- ◆ Maxwell relations give derivatives of entropy in convenient form