

Physical Chemistry

Lecture 17

Maxwell Relations

Spontaneity under arbitrary conditions

- ◆ Constant U and V
 $(\Delta S)_{U,V} \geq 0$
- ◆ Constant T and V
 $(\Delta A)_{T,V} \leq 0$
- ◆ Constant T and P
 $(\Delta G)_{T,P} \leq 0$
- ◆ Must calculate changes to make predictions

Free-energy changes

- ◆ Helmholtz free energy, A

$$dA = -SdT - PdV$$

- ◆ Gibbs free energy, G

$$dG = -SdT + VdP$$

- ◆ Must know how entropy depends on temperature to evaluate free-energy change

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

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

Evaluation by integration

- ◆ Evaluate changes of a function such as A or G in a process requires evaluating an integral of a derivative

$$\Delta A = -\int_{T_1}^{T_2} S(T)dT - \int_{V_1}^{V_2} P(V)dV$$

$$\Delta G = -\int_{T_1}^{T_2} S(T)dT + \int_{P_1}^{P_2} V(P)dP$$

Maxwell relation from Helmholtz energy

- ◆ By definition $dA = -SdT - PdV$

- ◆ Equality of crossed second partial derivatives of the state function, A

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right)_T$$

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

Maxwell relation from Gibbs energy

- ◆ By definition $dG = -SdT + VdP$

- ◆ Equality of crossed second partial derivatives of the state function, G

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T$$

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

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

Evaluating entropy at a temperature

- ◆ By definition

$$S(T, P) = S(T_{ref}, P) + \int_{T_{ref}}^T \left(\frac{\partial S}{\partial T} \right)_P dT$$

$$= S(T_{ref}, P) + \int_{T_{ref}}^T \frac{C_p(T)}{T} dT$$

- ◆ Determined by the way the heat capacity changes
- ◆ Must specify entropy at the reference temperature (Third Law)

Evaluating entropy at a pressure

- ◆ By definition of the change in a state function

$$S(T, P) = S(T, P_{ref}) + \int_{P_{ref}}^P \left(\frac{\partial S}{\partial P} \right)_T dP$$

$$= S(T, P_{ref}) - \int_{P_{ref}}^P \left(\frac{\partial V}{\partial T} \right)_P dT$$

- ◆ Evaluation by change of volume

$$S(T, V) = S(T, V_{ref}) + \int_{V_{ref}}^V \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$= S(T, V_{ref}) + \int_{V_{ref}}^V \left(\frac{\partial P}{\partial T} \right)_V dT$$

Standard molar entropies at 298.15 K

- ◆ Evaluate entropies by numerical integration of heat capacities

Solid	S° (J/K)	Liquid	S° (J/K)	Gas	S° (J/K)
Ag	42.55	Br ₂	152.2	H ₂	130.7
AgCl	96.2	H ₂ O	69.9	N ₂	191.6
Graphite	5.74	Hg	76.0	O ₂	205.1
Diamond	2.377	CH ₃ OH	126.8	CO ₂	213.7
I ₂	116.1	C ₂ H ₅ OH	160.7	Ar	154.9
Hg ₂ Cl ₂	196.	C ₆ H ₆	173.	Xe	169.7

Internal energy derivatives

- ◆ For a reversible process

$$dU = TdS - PdV$$

- ◆ Replace entropy differential by definition

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

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

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

- ◆ The last substitution uses a Maxwell relation

Identifying partial derivatives

- ◆ Compare equation to standard form

$$\left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \Rightarrow \left(\frac{\partial S}{\partial T} \right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

- ◆ Gives evaluable forms for derivatives

Other forms of work

- ◆ Stretching an elastic network

$$dw_{elastic} = fdl$$

- ◆ Moving charge against an electric potential

$$dw_{electric} = VdQ$$

- ◆ Magnetizing a material

$$dw_{magnetic} = BdM$$

- ◆ Creating a surface

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

Summary

- ◆ Free-energy changes specify spontaneity
 - $(dA)_{T,V} \leq 0$
 - $(dG)_{T,P} \leq 0$
- ◆ Must calculate the changes, ΔA and/or ΔG , to determine spontaneity of a process
- ◆ Maxwell relations provide connection between derivatives to allow proper integration