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Reading HW #6

Macrosopic Chemistry

5.12 : Using the fact that  $S$  is a state function to determine dependence of  $S$  on  $V$  and  $T$

$$dS = \frac{1}{T} dV + \frac{P}{T} dV$$

\* since  $\frac{1}{T}$  &  $\frac{P}{T} > 0$ , the entropy of system increases with internal energy at constant volume

↳ and increases with the volume at constant internal energy

↳ since internal energy usually not experimentally calculated more useful to obtain equation based of dependence of  $dS$  on  $V$  and  $T$

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

$$\hookrightarrow dS = \frac{1}{T} \left[ CV dT + \left(\frac{\partial V}{\partial T}\right)_P dP \right] + \frac{P}{T} dV = \frac{CV}{T} dT$$

$$+ \frac{1}{T} \left[ P + \left(\frac{\partial V}{\partial T}\right)_P \right] dV$$

Temperature dependence of entropy at constant volume

$$\hookrightarrow dS = \frac{CV}{T} dT, \text{ constant } V$$

can say

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

\* Constant  $T \uparrow$   
of constant  $V$

+ constant  $V \uparrow$   
of constant  $T$

$$\left(\frac{\partial S}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right)_T = \frac{1}{T} \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$$

$$\left(\frac{\partial S}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = \frac{1}{T} \left[\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V\right]$$

$$- \frac{1}{T^2} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

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

Dependence of entropy on volume under constant temperature:

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

$\hookrightarrow$  we can now express  $dS$  in terms of  $dT$  and  $dV$  as

$$dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV$$

$\hookrightarrow$  Inverse

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT + \int_{V_i}^{V_f} \frac{\beta}{\kappa} dV$$

(5p)

## 5.13 The Dependence of S on T and P

\* varies with T and P

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$\hookrightarrow \text{know } dV = TdS - PdV = dH - PdV - Vdp$$

so

$$ds = \frac{1}{\Gamma} dH - \frac{v}{\Gamma} dp$$

↳ suggestive expression for  $\partial H$  in

$$\delta H = \left(\frac{\partial H}{\partial r}\right)p\delta r + \left(\frac{\partial H}{\partial p}\right)_r \delta p = \left(p\delta r + \left(\frac{\partial H}{\partial p}\right)_r\right)\delta p$$

$$\hookrightarrow \text{Ges } ds = \left( \frac{\rho}{T} dT + \frac{1}{T} \left[ \frac{\partial H}{\partial \rho} \right]_T - v \right) d\rho = \left( \frac{\partial S}{\partial T} \right)_\rho dT + \left( \frac{\partial S}{\partial \rho} \right)_T d\rho$$

$\hookrightarrow$  coefficients of  $J_T$  and  $J_P$  must be same

$$\text{So... } \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \text{ and } \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[ \left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

- ratio  $(p/T)$  positive for all substances
  - can conclude  $s$  is monotonically increasing function of the temperature

Direc<sup>o</sup> comparison for  $(\cos/\sin)_P$  and  $(\cos/\sin)_T$

$$\left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial p}\right)_T\right)_p = \left(\frac{\partial}{\partial p} \left(\frac{\partial S}{\partial T}\right)_p\right)_T$$

$$\left( \frac{\partial}{\partial p} \left( \frac{\partial S}{\partial T} \right)_p \right)_T = \frac{1}{T} \left( \frac{\partial^2 S}{\partial p^2} \right)_T = \frac{1}{T} \cdot \left( \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial T} \right)_p \right)_T$$

$$\left\{ \left( \frac{\partial}{\partial r} \left( \frac{\partial S}{\partial p} \right)_T \right)_p = \frac{1}{r} \left[ \left( \frac{\partial}{\partial r} \left( \frac{\partial u}{\partial p} \right)_T \right)_p - \left( \frac{\partial u}{\partial r} \right)_p \right] \frac{1}{r^2} \left[ \left( \frac{\partial u}{\partial p} \right)_T - v \right] \right\}$$

$$\text{Together yield: } \frac{1}{T} \left( \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial p} \right)_S \right)_P = \frac{1}{T} \left[ \frac{\partial}{\partial T} \left( \frac{\partial H}{\partial P} \right)_S \right]_P - \left( \frac{\partial^2 V}{\partial T^2} \right)_P - \frac{1}{T^2} \left[ \left( \frac{\partial H}{\partial P} \right)_S \right]$$

$$\text{Simplicity: } \left(\frac{\partial Y}{\partial P}\right)_T - v = -T \left(\frac{\partial V}{\partial T}\right)_P \rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -v\beta$$

$$\hookrightarrow \text{concluise } DS = \frac{P}{T} dT - V\beta dP \rightarrow DS = \int_{T_i}^{T_f} \frac{CP}{T} dT - \int_{P_i}^{P_f} V\beta dP$$

## 6.1 The Gibbs Energy and the Helmholtz Energy

$$\Delta S + \Delta S_{\text{surrounding}} > 0$$

\* Gibbs and Helmholtz energies can calculate maximum work extracted from a chemical reaction

Clausius Inequality (governing spontaneity)

$$\hookrightarrow T\Delta S \geq \Delta Q$$

↪ satisfied only for reversible process cause  $\Delta Q = \Delta U - \Delta W$

$$T\Delta S \geq \Delta U - \Delta W, \text{ or } -\Delta U + \Delta W + T\Delta S \geq 0$$

↪ work arises from a volume change in the system and nonexpansion work

$$\hookrightarrow -\Delta U - P_{\text{external}} \Delta V + \Delta W_{\text{nonexpansion}} + T\Delta S \geq 0$$

State Functions:  $U, V, S$ , and  $T$

path Functions:  $P_{\text{external}}, \Delta V$ , and  $\Delta W_{\text{nonexpansion}}$

\* Isolated system,  $w=0$  and  $\Delta V=0$

$$\hookrightarrow \Delta S \geq 0$$

$$-\Delta U + T\Delta S \geq -\Delta W_{\text{expansion}} - \Delta W_{\text{nonexpansion}} \text{ or equivalently}$$
$$\Delta(U - TS) \leq \Delta W_{\text{expansion}} + \Delta W_{\text{nonexpansion}}$$

Helmholtz energy, abbreviated  $A'' \Rightarrow A = U - TS$

$$\hookrightarrow \Delta A - \Delta W_{\text{expansion}} - \Delta W_{\text{nonexpansion}} \leq 0$$

$$\hookrightarrow \Delta W_{\text{total}} = \Delta W_{\text{expansion}} + \Delta W_{\text{nonexpansion}} \geq \Delta A$$

•  $U$  = internal energy (Joules)

•  $T$  = absolute temperature (Kelvins)

•  $S$  = entropy ( $J/K$ )

•  $A$  = Helmholtz free energy (Joules)

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

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

Differentials

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + Vdp = TdS + Vdp$$

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

$$dG = TdS + Vdp - TdS - SdT = -SdT + Vdp$$

Internal Energy:  $U(S, V)$

Enthalpy:  $H(S, P)$

Helmholtz energy:  $A(T, V)$

Gibbs energy:  $G(T, P)$

} natural variables

Since  $U, H, A$ , and  $G$  are state functions can rewrite all

$$dU = TdS - PdV = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

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

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

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

$\Delta V$  exact differential:

$$\left( \frac{\partial}{\partial V} \left( \frac{\partial U(s, v)}{\partial s} \right)_V \right)_S = \left( \frac{\partial}{\partial S} \left( \frac{\partial U(s, v)}{\partial v} \right)_S \right)_V$$

Maxwell relations: derivable from symmetry of second derivatives and from definitions of thermodynamic potentials

$$(1) \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$(2) \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

$$(3) \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V = \frac{P}{T}$$

$$(4) - \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P = V\beta$$

6.3 The Dependence of The Gibbs and Helmholtz Energies on  $P, V$  and  $T$

$A$  changes with  $T$  and  $V$

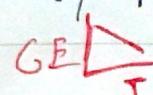
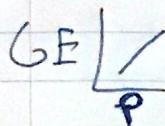
$$\left( \frac{\partial A}{\partial T} \right)_V = -S \text{ and } \left( \frac{\partial A}{\partial V} \right)_T = -P$$

\*  $S$  and  $P$  always take on positive values so Helmholtz energy of pure substance decreases as  $T$  or volume increases

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

\* Gibbs energy  $\downarrow$  with increasing  $T$

\* Gibbs energy  $\uparrow$  with increasing pressure



Makroscopic change in P at constant T

$$\hookrightarrow \int_{p_0}^P dG = G(T, P) - G^\circ(T, P_0) \approx \int_{p_0}^P v dp'$$

Liquids & Solids

$$G(T, P) = G^\circ(T, P_0) + \int_{p_0}^P v dp' \approx G^\circ(T, P_0) + v(P - P_0)$$

\* independent over a limited range in P

Gaseous system

$$G(T, P) = G^\circ(T) + \int_{p_0}^P v dp' = G^\circ(T) + \int_{p_0}^P \frac{MR}{P} \frac{dp'}{P} = G^\circ(T) + nRT \ln \frac{P}{P_0}$$

Dependence of G on T

$$\hookrightarrow \left( \frac{\partial [G/T]}{\partial T} \right)_P = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P + G \frac{\partial (1/T)}{\partial T}$$

$$= \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_P - \frac{G}{T^2} = \frac{S}{T} - \frac{H}{T^2} = - \frac{H + TS}{T^2} = - \frac{H}{T^2}$$

Gibbs-Helmholtz Equation

$$\frac{\partial (1/T)}{\partial T} = -\frac{1}{T^2}$$

$$\hookrightarrow \left( \frac{\partial [G/T]}{\partial [1/T]} \right)_P = \left( \frac{\partial [G/T]}{\partial T} \right)_P \cdot \left( \frac{\partial T}{\partial [1/T]} \right) \\ = -\frac{H}{T^2} (-T^2) = H$$

$$\text{Reflux G by } \Delta G \quad \int_{T_1}^{T_2} \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial T} \right) = \int_{T_1}^{T_2} \frac{\partial H}{\partial T} \left( \frac{1}{T} \right) \\ \hookrightarrow \frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$