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Reading HW #6

03/20/2020

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

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

$$dS = \frac{1}{T} [C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV] + \frac{P}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

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

The dependence of entropy on volume under constant temp conditions

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

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

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

5.13 The dependence of  $S$  on  $T$  and  $P$

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

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

always positive

-  $S$  is a monotonically increasing function of  $T$

$$\left. \begin{aligned} \left(\frac{\partial S}{\partial P}\right)_T &= - \left(\frac{\partial V}{\partial T}\right)_P = -V\beta \\ dS &= \frac{C_P}{T} dT - V\beta dP \end{aligned} \right\} \Delta S = \int_{T_i}^{T_f} \frac{C_P}{T} dT - \int_{P_i}^{P_f} V\beta dP$$



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6.1

## The Gibbs Energy and the Helmholtz Energy

- formulating spontaneity in terms of Gibbs and Helmholtz energies has the advantage that spontaneity and equilibrium can be defined using only properties of the system
- Clausius inequality:

$$TdS \geq dq$$

$$TdS \geq dU - \delta w \quad \text{or} \quad -dU + \delta w + TdS \geq 0$$

- $-dU + TdS \geq -\delta w_{\text{exp}} - \delta w_{\text{nonexp}}$   
or

$$d(U - TS) \leq \delta w_{\text{exp}} + \delta w_{\text{nonexp}}$$

- Helmholtz energy (A):

$$dA - \delta w_{\text{exp}} - \delta w_{\text{nonexp}} \leq 0$$

$$dA \leq 0$$

$$dT = 0$$

$$dT \text{ and } dV = 0$$

- Gibbs energy (G):

$$dG - \delta w_{\text{nonexp}} \leq 0$$

$$dG \leq 0$$

$$dP = 0$$

$$dP \text{ and } dT = 0$$

\* Knowing  $\Delta A$  and  $\Delta G$  for the system alone is sufficient to predict the direction of natural change

- For macroscopic changes at constant P and T in which no expansion work is possible, the condition for spontaneity is  $\Delta G_R < 0$  where  $\Delta G_R = \Delta H_R - T\Delta S_R$

- at constant V and T,  $\Delta A_R < 0$  where

$$\Delta A_R = \Delta U_R - T\Delta S_R$$

- $\Delta U_R$  is an energetic contribution } for  $\Delta A_R$
- $T\Delta S_R$  is an entropic contribution }
- $\Delta H_R$  is an energetic contribution } for  $\Delta G_R$
- $T\Delta S_R$  is an entropic contribution }



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

- $U$  and  $H$  calculate changes in energy for processes
- $A$  and  $G$  calculate direction in which processes evolve and the max. work the rxns produce

- Definitions:

$$H = U + PV$$

$$A = U - TS$$

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

- Differentials:

$$dU = TdS - PdV$$

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

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

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

- Expressions:

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

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

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

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

### Maxwell Relations

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

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

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

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

## 6.3 The Dependence of Gibbs & Helmholtz energies on $P$ , $V$ , and $T$

- The Helmholtz energy of a pure substance decreases as either the temp or volume increases

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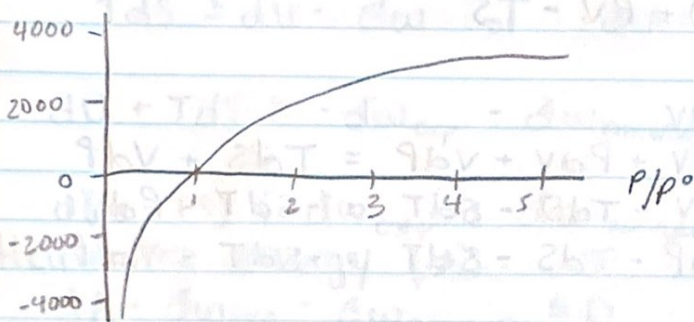
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- Gibbs energy decreases with increasing temp but Gibbs increases with increasing pressure
- For a macroscopic change in  $P$  at constant  $T$ :

$$\int_{P^0}^P dG = G(T, P) - G^0(T, P^0) = \int_{P^0}^P V dP'$$

$$G(T, P) = G^0(T) + \int_{P^0}^P V dP' = G^0(T) + \int_{P^0}^P \frac{nRT}{P'} dP' = G^0(T) + nRT \ln \frac{P}{P^0}$$

$[G_m(T, P) - G_m^0(T)]/J$



molar Gibbs energy of an ideal gas as a function of pressure at 298 K.

- Gibbs-Helmholtz Equation

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

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

or

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

$$\int_{T_1}^{T_2} d\left(\frac{\Delta G}{T}\right) = \int_{T_1}^{T_2} \Delta H d\left(\frac{1}{T}\right)$$

$$\frac{\Delta G(T_2)}{T_2} = \frac{\Delta G(T_1)}{T_1} + \Delta H(T_1) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$