

Chap. 7.8.

One - Component Sys.

7.1.

temp. of a sys = a measure of the potential or intensity of heat in the system.

pressure of a sys = a measure of its tendency toward movement

Chemical pot. " = " of the spec to leave the phase.

G-T-P to examine the equil<sup>n</sup>.

Gib

7.2. The variation of Gibbs f. E w/ T at const P.  
 - p = 1 atm T = 0°C. ice & water equil<sup>n</sup>.



$\Delta G = G_{H_2O(l)} - G_{H_2O(s)} = 0. \quad \text{at Transition.}$

(7.1)  $\therefore G_{H_2O(l)} = G_{H_2O(s)} \Rightarrow \text{molar free E.}$

For the sys. of ice + water w/ n moles of  $H_2O(s)$  (= n  $H_2O(s)$ )  
 (total)  $\pm$  molar. n moles of  $H_2O(l)$  (= n  $H_2O(l)$ )  
 the free E. of the sys.,  $G'$ ,

(7.2)  $G' = n_{H_2O(s)} \cdot G_{H_2O(s)} + n_{H_2O(l)} \cdot G_{H_2O(l)}$  > min. value for a system.

From (7.1) at 0°C, 1 atm, the  $G'$  is indep. of the proporti  
 of the water phase & the ice phase. (ratios)

- (5.25)  $dG = -SdT + VdP + \sum \mu_i dn_i$   
 at const T, P.  $dG = \sum \mu_i dn_i$   
 Integrate for min.  $G'$ ,  $G' = \sum \mu_i n_i$

4/16

but to have a... 2

the  
- for ice & water sys.

$$(7.3) \quad G' = \mu_{H_2O(s)} \cdot n_{H_2O(s)} + \mu_{H_2O(l)} \cdot n_{H_2O(l)}$$

Comparison of Gs. (7.2) & (7.3)

Chemical pot. of a species = Gibbs F.E./  
of the spe

$$\mu_{H_2O} = G_{H_2O}$$

$$\text{or } \mu_i = G_i(\text{phase})$$

from (5.16)  $\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i = G_i \rightarrow \left(\frac{\partial G'}{\partial n_i}\right)_{T,P} = \mu_i = G_i(\text{phase})$

$\therefore$  In a one-component sys.

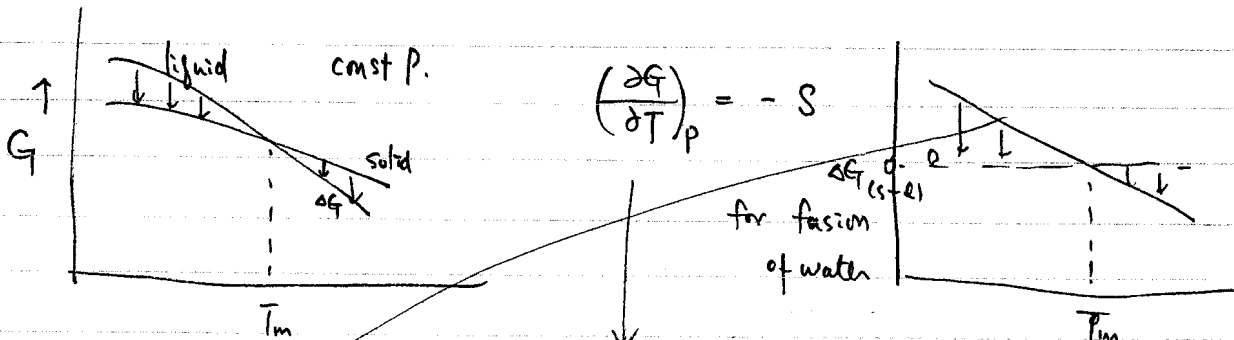
the chemical potential of a species in a particular state equals the Gibbs free Energy/mole of species in the particular state

intergrate. for the addition of of the  $\mu = \Delta G'$  for the at sys. resulting from the additive

- For the ice & water sys. at  $P=1$ ,  $T > 0^\circ\text{C}$ . 1 mole of it at const T.

$$\Delta G = G_{H_2O(l)} - G_{H_2O(s)} < 0 \rightarrow G_{H_2O(l)} < G_{H_2O(s)}$$

$$\text{if } T < 0 \rightarrow G_{H_2O(l)} > G_{H_2O(s)}$$



$$(6.12) \quad \left(\frac{\partial^2 G}{\partial T^2}\right)_P = -\left(\frac{\partial S}{\partial T}\right)_P = -\frac{C_p}{T}$$

slope.  $\left(\frac{\partial \Delta G}{\partial T}\right) = -\Delta S$  the entropy change in rx.

the slope = negative  $\rightarrow$  means  $S_{H_2O(l)} > S_{H_2O(s)}$

For

=> The state in which the solid and liquid phase of a one-comp. sy are in equil<sup>m</sup> w/ one another.

at const. T.P.  $G = H - TS$   $G(l) = H(l) - TS(l)$   
 $G(s) = H(s) - TS(s)$

∴ for the rxn  $s \rightarrow l$ .

$$\Delta G(s \rightarrow l) = \Delta H(s \rightarrow l) - T \Delta S(s \rightarrow l)$$

molar enthalpy & entropy

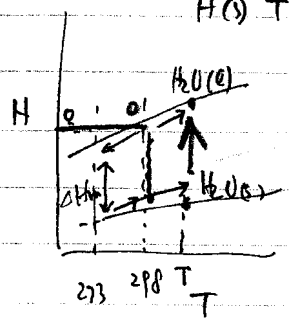
Since  $\Delta G(s \rightarrow l) = 0$  at  $T_m$ .

(7.4)  $\Delta H(s \rightarrow l) = T_m \Delta S(s \rightarrow l)$

= For  $H_2O$  figure 7.2, 7.3 (a, b) for convenience  $H(l)_{298} =$

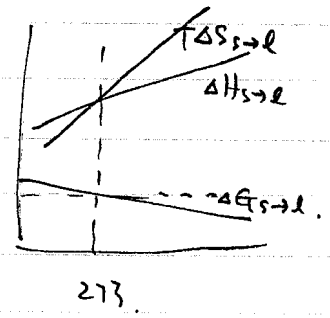
$$H(l)_T = \int_{298}^T C_{p(l)} dT = 77.4 (T - 298) \text{ joules/deg.}$$

$$H(s)_T = \int_{298}^{273} C_{p(s)} dT - \Delta H_m + \int_{273}^T C_{p(s)} dT$$



$$\Delta H(s \rightarrow l)_T = H(l)_T - H(s)_T$$

Similarly  $\Delta S_{s \rightarrow l, T} = S(l)_T -$



$$S(l)_T = S(l)_{298} + \int_{298}^T \frac{C_{p(l)}}{T} dT$$

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Above  $T_m$ , the Entropy contribution outweighs the enthalpy contribution to  $\Delta G$

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7.3. The variation of Gibbs f.E. w/ P at const. T.

a Mixture of ice & water at 0°C, 1 atm. as P ↑ than 1 atm.

the sys. try to be w/less

ice at 0°C a larger molar vol. than water. ∴ P ↑ cause melt of ice.

for the rxn.

$$\left(\frac{\partial G_{(l)}}{\partial P}\right)_T = V_{(l)}, \quad \left(\frac{\partial G_{(s)}}{\partial P}\right)_T = V_{(s)}$$

rate of increase of G, w.r.t. P = the molar vol. of the pl at

$$\left(\frac{\partial \Delta G_{(s \rightarrow l)}}{\partial P}\right)_T = \Delta V_{(s \rightarrow l)}$$

for water at 0°C.  $\Delta V_{s \rightarrow l} < 0$ . then ice melts as P ↑

7.4. Gibbs f.E. as a fn of T. & P.

Equil bet'n solid & liquid by varying T. P. together with

$$\Delta G_{(s \rightarrow l)} = 0 \quad \rightarrow \text{for this } G_{(s)} = G_{(l)}$$

$$[S_{(s)} - S_{(l)}] dT + [V_{(s)} - V_{(l)}] dP = 0$$

for a infinitesimal change.

$$dG_{(s)} = dG_{(l)}$$

$$= -S_{(l)} dT + V_{(l)} dP$$

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$$\left(\frac{dP}{dT}\right)_G = \frac{S_{(s)} - S_{(l)}}{V_{(s)} - V_{(l)}} = \frac{\Delta S_{(l-s)}}{\Delta V_{(l-s)}}$$

Clapeyron Equation

At equil  $\Delta G = 0 \rightarrow \Delta H = T \Delta S$

$$\therefore \left(\frac{dP}{dT}\right)_G = \frac{\Delta H}{T \Delta V} \quad (2.5)$$

Phase Equilib in a one-comp. sys.

(5)

ice + water.  $\Delta V_{(s \rightarrow l)} < 0$ , and  $\Delta H_{(s \rightarrow l)} > 0$ .

$\therefore \left(\frac{dP}{dT}\right)_g < 0$ . as  $P \uparrow$ ,  $T_m \downarrow$  ice skating.

of various solids, liquids

7.5 Equil<sup>m</sup> bet'n the vapor phase and a condensed phase.

If (2.5) used for vapor-condensed phase equilibria.

$$\Delta V = V_{\text{vap}} - V_{\text{cond}} = V_{\text{vap}}$$

$$\therefore (2.5) \rightarrow \left(\frac{dP}{dT}\right) = \frac{\Delta H}{TV_{\text{vap}}}$$

— molar latent heat of evap. + sub  
— assumed ideal gas.

$$\frac{dP}{dT} = \frac{P \Delta H}{RT^2} \rightarrow \frac{dP}{P} = \frac{\Delta H}{RT^2} dT$$

(2.6)

$$\boxed{d \ln P = \frac{\Delta H}{RT^2} dT}$$

(solid-vapor) Clausius-Clapeyron Eq.

i) if  $\Delta H \neq f(T)$  (<sup>but</sup> wrong!!) i.e.,  $G_p(\text{vapor}) = G_p(\text{condensed})$

(2.7) Integrate (2.6)

$$\boxed{\ln P = -\frac{\Delta H}{RT} + \text{const}} \quad !!$$

the saturated vapor pressure exerted by the condensed phase  
increases exponentially w/  $T \uparrow$ .

ii) ~~if  $\Delta H \neq f(T)$~~ . ~~if  $\Delta C_p \neq 0$~~ ,  $\Delta C_p \neq 0$ ,  $\Delta H \neq f(T)$ .

$$(6.9) \Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT$$

$$\therefore \Delta H_T = \Delta H_{298} + \Delta C_p (T - 298)$$

assumption.

$$(2.8) \boxed{\ln P = \frac{A}{T} + B \ln T + C}$$

7.6 Graphical Rep. of Phase Equil