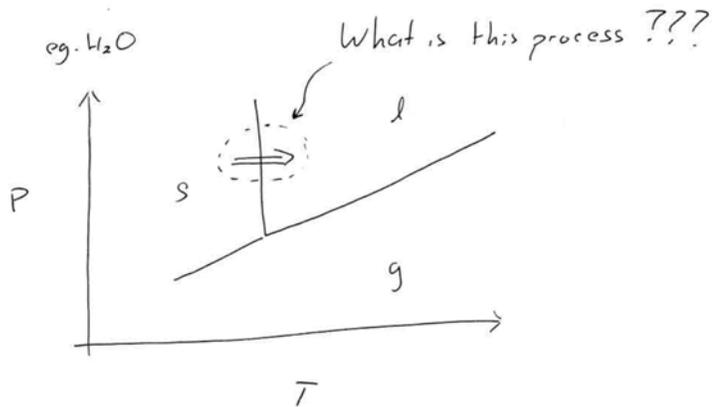


3.020 Lecture 10

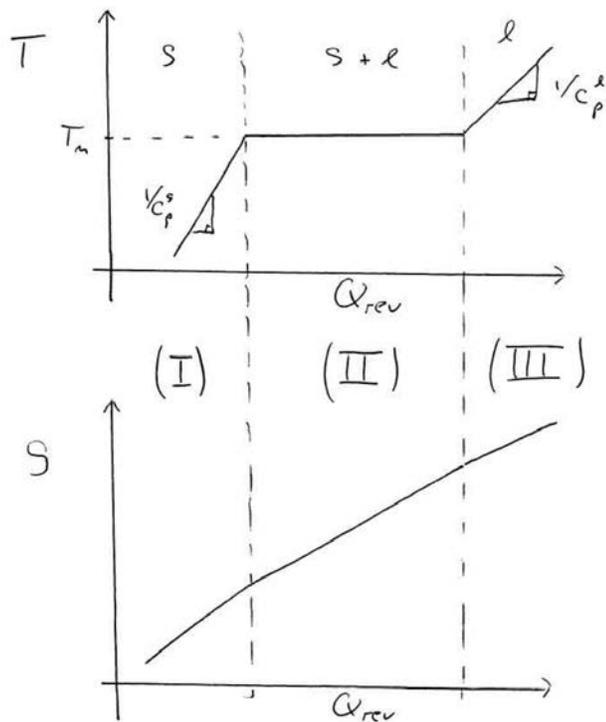
Prof. Rafael Jaramillo

1 Unary phase transformations



Solid \rightarrow liquid

- Breaking bounds
- Increasing enthalpy
- Increasing disorder
- Increasing entropy

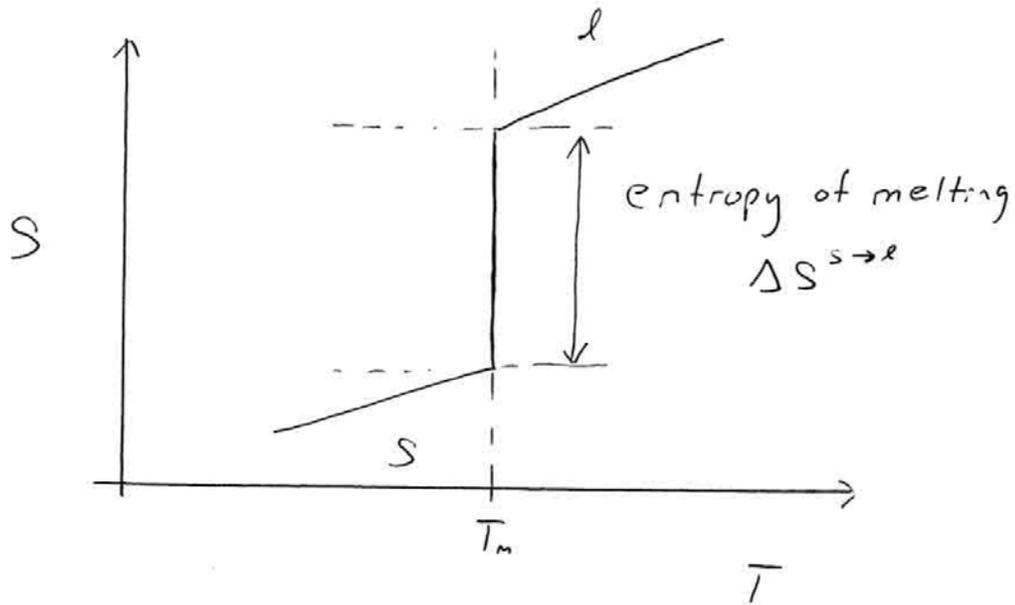


(I) Heating solid phase

(II) Melting solid \rightarrow liquid
at fixed $T = T_M$

(III) Heating liquid phase

recall $ds = \frac{\delta Q|_{rev}}{T}$



- Enthalpy (or “heat”) of melting

$$\Delta H^{s \rightarrow l} = \Delta Q_{rev}^{s \rightarrow l} = T_m \Delta S^{s \rightarrow l}$$

Higher-temp phase always has higher entropy

Consider $\alpha \leftrightarrow \beta$ coexistence at temp $T^{\alpha \rightarrow \beta}$

- Heating converts $\alpha \rightarrow \beta$

$$dn^\alpha = -dn^\beta < 0$$

- Heating increases entropy $dS = \frac{\delta Q|_{rev}}{T^{\alpha \rightarrow \beta}} > 0$
- Entropy is extensive $S' = n^\alpha S^\alpha + n^\beta S^\beta$

requires that $S^\beta > S^\alpha$



S^α, S^β : molar entropy of phases **intensive**

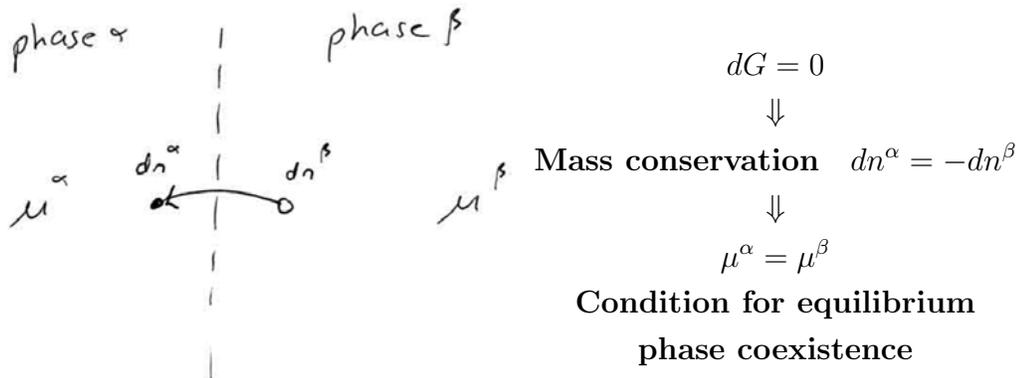
S' : total entropy of system **extensive**

2 Building unary phase diagrams

(1) Role of chemical potential

$$dG' = -S' dT + V' dP + \sum_k \mu^k dn^k$$

At fixed (T, P) , equilibrium condition is $dG = 0$



(2) What is chemical potential ?

$$\mu = \left. \frac{\partial G}{\partial n} \right|_{T,P} = \text{molar Gibbs free energy}$$

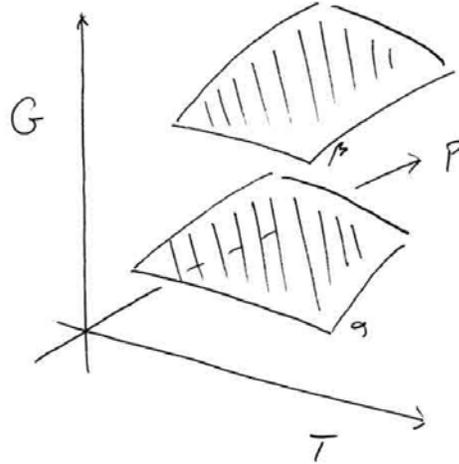
$$G'(T, P, n = 1) = \mu \quad G'(T, P, n) = n\mu$$

(3) Determining phase equilibrium-drawing phase diagrams

- (a) At each (P, T) , calculate μ for all possible phases
- (b) Equilibrium phase is the one with lowest $\mu(P, T)$
- (c) If multi phases have equal μ , then they can coexist

3 Chemical potential surfaces

- $\mu(T, P)$ is a surface over the (T, P) plane
- Each phase has its own surface

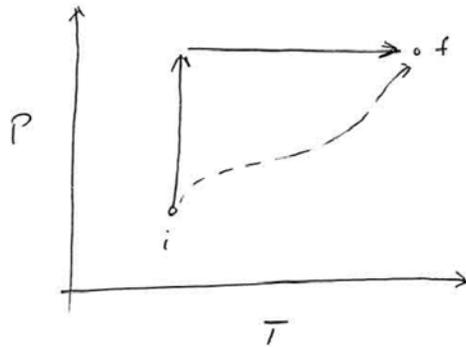


- Calculating $\Delta\mu$ for a change in temperature/pressure for a given phase

$$d\mu = -SdT + VdP$$

$$\Delta\mu = \int_i^f d\mu = \int_i^f dT(-S) + \int_i^f dPV$$

implicitly assumes that we have EoS for $S(T, P), V(T, P)$



- In general we don't know $S(T, P)$ and $V(T, P)$, but we can calculate from S^0, V^0 at standard conditions and differential forms :

$$dS = \frac{C_P}{T}dT - V\alpha dP$$

$$dV = V\alpha dT - V\beta dP$$

S, V are also surfaces over the (T, P) plane

- Calculating $\Delta\mu$ for a change of phase at fixed (T, P)

$$\Delta\mu = \Delta G = \Delta H - T\Delta S$$

- At phase coexistence, $\Delta\mu = 0$, $\Delta H = T\Delta S$
- Away from phase coexistence, can evaluate $\Delta H, \Delta S$ from standard values and differential forms:

$$dH = C_P dT + V(1 - T\alpha)dP$$

$$dS = \frac{C_P}{T} dT - V\alpha dP$$

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3.020 Thermodynamics of Materials
Spring 2021

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