

Chapter 5

Vapor-Solid Processes

April 27: Evaporation Processes

(Supplement to slides)

Evaporation/condensation Clapeyron equation: Gibbs free energy

$$G = H - TS = U + PV - TS \quad (5.1)$$

For two phases in equilibrium, along coexistence curve G changes the same way

$$dG_1 = dG_2,$$

$$V_1 dP_1 - S_1 dT_1 = V_2 dP_2 - S_2 dT_2,$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}.$$

For evaporation:

$$\Delta V \simeq V_{gas} = \frac{nRT}{P}$$

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

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

$$\ln P = -\frac{\Delta H}{nRT} + B. \quad (5.2)$$

With $\Delta H = mT + b$, get another term $+C \ln T$.

Equilibrium pure vapor pressure: Clausius-Clapeyron equation, one form:

$$\log_{10} p_v = -\frac{A}{T} + B + C \log_{10} T (+DT), \quad (5.3)$$

units: torr, conversion factor. If not pure, then mult by activity. Either way, multiply material flux J by ΔH_{vap} for heat flux influence.

Evaporation rate into a vacuum: Langmuir equation

$$J = \frac{p_v}{\sqrt{2\pi MRT}}. \quad (5.4)$$

Here the units should work, go through.

Evaporation ratio: dilute solution of B in A

$$ER_B = \frac{\text{wt}\%B_{\text{vapor}}/\text{wt}\%A_{\text{vapor}}}{\text{wt}\%B_{\text{melt}}/\text{wt}\%A_{\text{melt}}} \quad (5.5)$$

This ratio will be equal to the equivalent ratio of mole fractions, and the ratio of mole fractions in the vapor is in turn equal to the ratio of Langmuir evaporation rates (equation ??), so the evaporation ratio can be rewritten as

$$ER_B = \frac{p_{vB}}{X_B \sqrt{M_B}} \frac{X_A \sqrt{M_A}}{p_{vA}} \quad (5.6)$$

where X_i represents the mole fraction of species i in the melt, p_{vi} its vapor pressure, and M_i its molecular weight. Assuming titanium activity roughly follows Raoult's law, its vapor pressure is the product of the vapor pressure in its pure state and mole fraction in the melt, so we rewrite the evaporation ratio again as

$$ER_B = \frac{p_{vB}}{X_B \bar{p}_{vA}} \sqrt{\frac{M_A}{M_B}} \quad (5.7)$$

where \bar{p}_{vi} represents the vapor pressure of pure species i . We then assume Henrian behavior and use the definition of the activity coefficient $p_{vB} = \gamma_B \bar{p}_{vB} X_B$ to arrive at

$$ER_B = \gamma_B \frac{\bar{p}_{vB}}{\bar{p}_{vA}} \sqrt{\frac{M_A}{M_B}} \quad (5.8)$$

Evaporation into gas: boundary layer, $J = h_D(C_s - C_{bulk})$.

Also for evaporation, heat flux from gas, plasma, radiation incl. laser (below), electron beam, etc. Condensation releases a lot of heat!