Thermodynamics of Materials

15th Lecture

2007. 5. 7 (Wednesday)

Thermodynamics of Chemical Vapor Deposition

How do we define the irreversibility criterion for deposition in CVD?

How about in PVD?

Transition between condensed phases
⇒ solid to liquid, solid (α) to solid (β)

$$\Delta G^{S\to L} = \Delta H^{S\to L} - T\Delta S^{S\to L}$$

⇒ close system

Transition between condensed and gas phases
⇒ solid to gas, gas to solid

$$dG = SdT - VdP + \sum \mu_j n_j$$
$$= \sum \mu_j n_j \quad \text{at constant T and P}$$

⇒ open system

What is the driving force for wet clothes to dry?

$$\Delta\mu_{H_2O}^{liquid\to gas} = \mu_{H_2O}^{gas} - \mu_{H_2O}^{liquid}$$
$$= \mu_{H_2O,gas}^{o} + RT\ln p_{H_2O}^{gas} - \left(\mu_{H_2O,gas}^{o} + RT\ln p_{H_2O}^{eq}\right)$$
$$= RT\ln p_{H_2O}^{gas} - RT\ln p_{H_2O}^{eq} = -RT\ln\left(\frac{p_{H_2O}^{eq}}{p_{H_2O}^{gas}}\right)$$

$$\alpha = \frac{p_{H_2O}^{eq}}{p_{H_2O}^{gas}} : \text{ Supersaturation Ratio for Evaporation}$$

$$\Delta\mu_{Cu}^{liquid\to gas} = -RT\ln\alpha : \text{ Driving Force for Evaporation}$$

What is the driving force for precipitation when the water vapor is supercooled from 300 K to 290 K?

$$\Delta u^{300K \to 290K} = -RT \ln\left(\frac{P_{300}}{P_{290}^{eq}}\right)$$

$$T = 290\ K$$

Assuming that the water vapor behaves like ideal gas.

→ Identical to Driving Force in PVD

Driving Force for Deposition in PVD
ex) Thermal Evaporation of Cu

$$\Delta \mu_{Cu}^{gas \to solid} = \mu_{Cu}^{solid} - \mu_{Cu}^{gas}$$

$$= \mu_{Cu,gas}^{o} + RT \ln p_{Cu}^{eq} - \left(\mu_{Cu,gas}^{o} + RT \ln p_{Cu}^{gas}\right)$$

$$= RT \ln p_{Cu}^{eq} - RT \ln p_{Cu}^{gas} = -RT \ln\left(\frac{p_{Cu}^{gas}}{p_{Cu}^{eq}}\right)$$

$\alpha = \frac{p_{Cu}^{gas}}{p_{Cu}^{eq}}$: *Supersaturation Ratio for Deposition*

$\Delta \mu_{Cu}^{gas \to solid} = -RT \ln \alpha$: *Driving Force for Deposition*

T : substrate temperature

Chemical Vapor Deposition

Precipitation of a solid phase from chemical reactions in the gas phase

Physical Vapor Deposition → **No chemical reactions**

$$2H_2 + O_2 \rightarrow 2H_2O(ice)$$

$$A + B \Rightarrow C_s + D$$

Find the expression for supersaturation and driving force for deposition.

$$\alpha = \frac{P_A^i P_B^i}{P_A^f P_B^f} \qquad \Delta\mu = -RT\ln\alpha$$

Usually very high value of α

When 'D' is supplied,

$$\alpha = \frac{P_A^i P_B^i P_D^f}{P_A^f P_B^f P_D^i} \qquad \Delta\mu = -RT\ln\alpha$$

Is this thermodynamic scheme correct?

$$A + B \Rightarrow C_s + D$$

A,B: Reactants, C, D : Products

C_s: deposition species

$$\mu_A^i = \mu_A^s + RT\ln P_A^i$$
$$\mu_B^i = \mu_B^s + RT\ln P_B^i$$

Initially, C and D are absent.

$$\mu_C^i = \mu_C^s + RT\ln(0) = -\infty$$
$$\mu_D^i = \mu_D^s + RT\ln(0) = -\infty$$

$$A + B \Rightarrow C_s + D$$

Driving force for forward reaction = ?

$$\Delta\mu = \sum\left(\mu_j^{\text{right side}} - \mu_j^{\text{left side}}\right)$$
$$= \mu_C^i + \mu_D^i - \mu_A^i - \mu_B^i$$
$$= \mu_C^s + RT\ln P_C^i + \mu_D^s + RT\ln P_D^i$$
$$-\mu_A^s - RT\ln P_A^i - \mu_B^s - RT\ln P_B^i$$
$$= \Delta\mu^s + RT\ln\left(\frac{P_C^i \; P_D^i}{P_A^i \; P_B^i}\right)$$

$$\Delta\mu = \Delta\mu^s + RT\ln\left(\frac{0}{P_A^i \; P_B^i}\right) = -\infty$$