

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)

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

⇒ close system

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

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

⇒ open system

What is the driving force for wet clothes to dry?

$$\begin{aligned} \Delta \mu_{H_2O}^{liquid \rightarrow gas} &= \mu_{H_2O}^{gas} - \mu_{H_2O}^{liquid} \\ &= \mu_{H_2O, gas}^0 + RT \ln p_{H_2O}^{gas} - \left(\mu_{H_2O, gas}^0 + RT \ln p_{H_2O}^{eq} \right) \\ &= RT \ln p_{H_2O}^{gas} - RT \ln p_{H_2O}^{eq} = -RT \ln \left(\frac{p_{H_2O}^{eq}}{p_{H_2O}^{gas}} \right) \end{aligned}$$

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

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

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

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

$$T = 290 \text{ K}$$

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**

$$\begin{aligned} \Delta \mu_{Cu}^{gas \rightarrow solid} &= \mu_{Cu}^{solid} - \mu_{Cu}^{gas} \\ &= \mu_{Cu, gas}^o + RT \ln p_{Cu}^{eq} - \left(\mu_{Cu, gas}^o + RT \ln p_{Cu}^{gas} \right) \\ &= RT \ln p_{Cu}^{eq} - RT \ln p_{Cu}^{gas} = -RT \ln \left(\frac{p_{Cu}^{gas}}{p_{Cu}^{eq}} \right) \end{aligned}$$

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

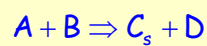
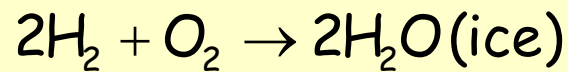
$$\Delta \mu_{Cu}^{gas \rightarrow solid} = -RT \ln \alpha : \text{Driving Force for Deposition}$$

T : substrate temperature

Chemical Vapor Deposition

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

Physical Vapor Deposition → No chemical reactions



Find the expression for supersaturation and driving force for deposition.

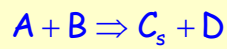
$$\alpha = \frac{p_A^i p_B^i}{p_A^f p_B^f} \quad \Delta\mu = -RT \ln \alpha$$

Usually very high value of α

When 'D' is supplied,

$$\alpha = \frac{p_A^i p_B^i p_D^f}{p_A^f p_B^f p_D^i} \quad \Delta\mu = -RT \ln \alpha$$

Is this thermodynamic scheme correct?



A, B: Reactants, C, D : Products

C_s : deposition species

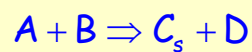
$$\mu_A^i = \mu_A^s + RT \ln P_A^i$$

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

Initially, C and D are absent.

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

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



Driving force for forward reaction = ?

$$\Delta\mu = \sum (\mu_j^{\text{right side}} - \mu_j^{\text{left side}})$$

$$= \mu_C^i + \mu_D^i - \mu_A^i - \mu_B^i$$

$$= \mu_C^s + RT \ln P_C^i + \mu_D^s + RT \ln P_D^i$$

$$- \mu_A^s - RT \ln P_A^i - \mu_B^s - RT \ln P_B^i$$

$$= \Delta\mu^s + RT \ln \left(\frac{P_C^i P_D^i}{P_A^i P_B^i} \right)$$

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