Thermodynamics of Materials

6th Lecture

2008. 3. 19 (Wed.)

$$G = H - TS = E + PV - TS$$

$$\begin{aligned} dG &= dE + PdV + VdP - TdS - SdT \\ &= dQ - PdV + PdV + VdP \\ &\quad - Td_eS - Td_iS - SdT \\ &= Td_eS - Td_eS - Td_iS \quad \text{at const. } T \text{ \& } P \\ &= -Td_iS \quad \text{at const. } T \text{ \& } P \end{aligned}$$

$$dG = -Td_iS \le 0 \qquad \text{at const. } T \text{ \& } P$$

$dG = -Td_iS \leq 0$ at const. T & P

$dF = -Td_iS \leq 0$ at const. T & V

$dE = -Td_iS \leq 0$ at const. S & V

$dH = -Td_iS \leq 0$ at const. S & P

Why the term "free" energy?

$$dS_{total} = dS_{sys} + dS_{surr}$$
$$= dS_e + dS_i - dS_e$$
$$= dS_i \rightarrow \text{상쇄되고 남은 엔트로피}$$

$dG = -TdS_i \rightarrow$ 상쇄되고 남은 에너지

$\rightarrow$ *Available Energy*

$\rightarrow$ *Free Energy*

$$\Delta G = \Delta H - \Delta(TS) = \Delta H - T\Delta S - S\Delta T$$
$$= \Delta H - T\Delta S \text{ at const. } T \& P$$

$$\Delta G = \Delta H - T\Delta S$$
$$= T\Delta S_e - T(\Delta S_e + \Delta S_i)$$
$$= -T\Delta S_i \leq 0$$

$\therefore \Delta H$와 ΔS만 구하면 된다.

$$\Delta H = \int C_p dT \qquad \Delta S = \int \frac{C_p}{T} dT$$

$\therefore C_p$의 온도의존성만 알면,
주어진 반응의 irreversibility 방향과
그 구동력의 크기를 결정할 수 있다.

C_p 에 관한 더 자세한 것은 나중에 다룸

$$dG = dH - d(TS) = -SdT + VdP$$

$\Delta G = \Delta H - T\Delta S$ and $dG = -SdT + VdP$

이 두 식은 어떻게 다른가?

이 두 식에서 G는 어떻게 다른가?

Homework

$dG = -SdT + VdP$

이식을 이용해서 앞의 문제를 풀어라.

At a pressure of 1 atm the equilibrium melting temperature of lead is 600 K, and, at this temperature, the latent heat of melting of lead is 4810 J/mole. Calculate Gibbs free energy change when 1 mole of supercooled liquid lead spontaneously freezes at 590 K and 1 atm pressure.

The constant-pressure molar heat capacity of liquid lead, as a function of temperature, at 1 atm pressure is given by

$$C_{p(l)} = 32.4 - 3.1 \times 10^{-3} T \ \ J/K$$

and the corresponding expression for solid lead is

$$C_{p(s)} = 23.6 + 9.75 \times 10^{-3} T \ \ J/K$$

$$dG = -SdT + VdP = -SdT$$

$$S_{Pb(l)} = \int \frac{C_{p,Pb(l)}}{T} dT$$

$$= \int \left(\frac{32.4}{T} - 3.1\times10^{-3} \right) dT = 32.4 \ln T - 3.1\times10^{-3} T + C_l$$

$$\Delta G_{b\to a} = \int_b^a -SdT = \int_{600K}^{590K} \left(-32.4 \ln T + 3.1\times10^{-3} T - C_l \right) dT$$

$$\Delta G_{b\to a} = \left[-32.4\left(T \ln T - T \right) + \frac{3.1\times10^{-3} T^2}{2} - C_l T \right]_{600}^{590}$$

$$= -102306.8674 + 104358.3125 = 2051.445 + 10C_l$$

혹은 $= 2069.89 - 18.445 = 2051.445 + 10C_l$

$$\Delta G_{c\to d} = \int_c^d -SdT = -\int_{600K}^{590K} \left(23.6 \ln T + 9.75\times10^{-3} T + C_s \right) dT$$

$$\Delta G_{c\to d} = -\left[23.6\left(T \ln T - T \right) + \frac{9.75\times10^{-3} T^2}{2} + C_s T \right]_{600}^{590}$$

$$= -\left(76609.8137 - 78175.5239 \right) = 1565.7102 + 10C_s$$

혹은 $= 1507.6977 + 58.0125 = 1565.7102 + 10C_s$

$$\Delta G_{a\to d} = 1565.7102 + 10C_s - 2051.445 - 10C_l$$

$$= 485.7 - 10\left[C_l - C_s \right]$$

$$S_{Pb(l)}(600K) = 32.4\ln T - 3.1\times10^{-3}T + C_l \Big]_{600K}$$
$$S_{Pb(s)}(600K) = 23.6\ln T + 9.75\times10^{-3}T + C_s \Big]_{600K}$$

$$S_{Pb(l)}(600K) = 32.4\ln T - 3.1\times10^{-3}T + C_l \Big]_{600K}$$
$$S_{Pb(s)}(600K) = 23.6\ln T + 9.75\times10^{-3}T + C_s \Big]_{600K}$$

$$S_{Pb(l)}(600K) - S_{Pb(s)}(600K) = \frac{\Delta H_m}{T_m} = \frac{4810}{600} = 8.017$$

$$C_l - C_s = 56.6$$

$$\Delta G_{a\to d} = 485.7 - 10\left[C_l - C_s\right]$$
$$= 485.7 - 10\times56.6 = -80.3$$

$$cf)\ \Delta G = -T\Delta S_{total}$$
$$= -590\times0.137$$
$$= -80.83J$$

The First Law of Thermodynamics

Conservation of Energy

$$\Delta E = \Delta Q - \Delta W$$

The Second Law of Thermodynamics

?

2법칙을 1법칙 만큼 확실하게 이해하면 된다.

다음 서술 중에서 엔트로피 효과와 관련된 것은 어느 것인가?

㉠ 서로 다른 두 종류의 기체는 혼합된다.
㉡ 열 에너지는 온도가 높은 곳에서 낮은 곳으로 전달된다.
㉢ 물과 기름을 한 용기에 넣고 흔들어 혼합하여도 둘은 섞이지 않고 분리된다.

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Ludwig Boltzmann (1844-1906)

Boltzmann's atom
David Lindley, The Free Press 2001.

http://www.corrosion-doctors.org/Biographies/BoltzmannBio.htm

Argument between Boltzmann and Ostwald in1895

'Boltzmann was seconded by Felix Klein.
The battle between Boltzmann and Ostwald resembled the battle of the bull
with the supple fighter.
However, this time the bull was victorious ... .
The arguments of Boltzmann carried the day.
We, the young mathematicians of that time,
were all on the side of Boltzmann ...'

http://www.timelinescience.org/resource/students/matter/boltzmn.htm

$S = k \log W$

http://www.timelinescience.org/resource/students/matter/boltzmn.htm