Thermodynamics of Materials

5th Lecture

2008. 3. 17 (Mon.)

$$dS - \frac{\delta Q}{T} \equiv \frac{\delta Q'}{T} \succ 0, (irreversible)$$

$$dS = \frac{\delta Q}{T} + \frac{\delta Q'}{T}$$

$\delta Q' = 0,$ reversible

$\delta Q' \succ 0,$ irreversible

$$\frac{\delta Q}{T} = d_e S, \quad \frac{\delta Q'}{T} = d_i S$$

δQ : exchange with the outside world

$\delta Q'$: irreversible change in the interior of the system

Kondepudi and Prigogine (1998)

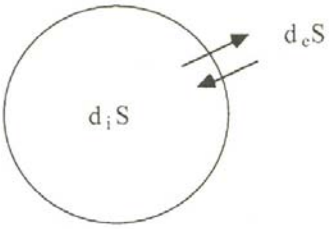


Figure 3.7 Entropy changes in a system consist of two parts: d_iS due to irreversible processes, and d_eS, due to exchange of energy and matter. According to the second law, the change d_iS is always positive. The entropy change d_eS can be positive or negative

$$dS = d_iS + d_eS$$

$d_iS = \text{entropy production}$ $\quad d_eS = \text{entropy flow}$

G. Jaumann, Math. Naturw. Klasse, 120 (1911) 385

$$dS = d_iS + d_eS$$

For closed systems, $d_eS = \frac{\delta Q}{T}; \; d_iS = \frac{\delta Q'}{T} \geq 0$

For isolated systems, $d_eS = 0; \; d_iS = \frac{\delta Q'}{T} \geq 0$

For open systems,

$$d_eS = \frac{\delta Q}{T} + \left(d_eS\right)_{matter}; \; d_iS = \frac{\delta Q'}{T} \geq 0$$

Universality of thermodynamic laws

Clausius in later years

1st Law: The Energy of the Universe is Constant.

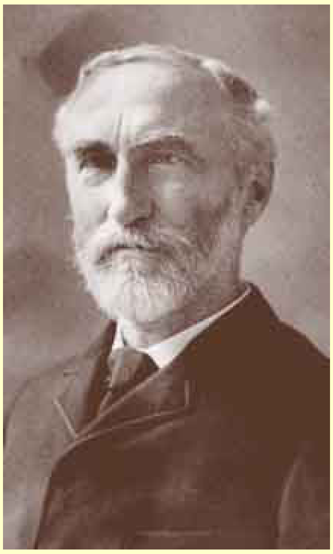
2nd Law: The Entropy tends to a Maximum.

Kelvin

“The Heat Death of the Universe”

Kelvin measured the rate at which heat is radiated from the Earth’s surface and predicted that 2,000 years in the future, the Earth will become ice cold and unable to support life.

Josiah Willard Gibbs (1839-1903)



On the Equilibrium of Heterogeneous Substances (1876)

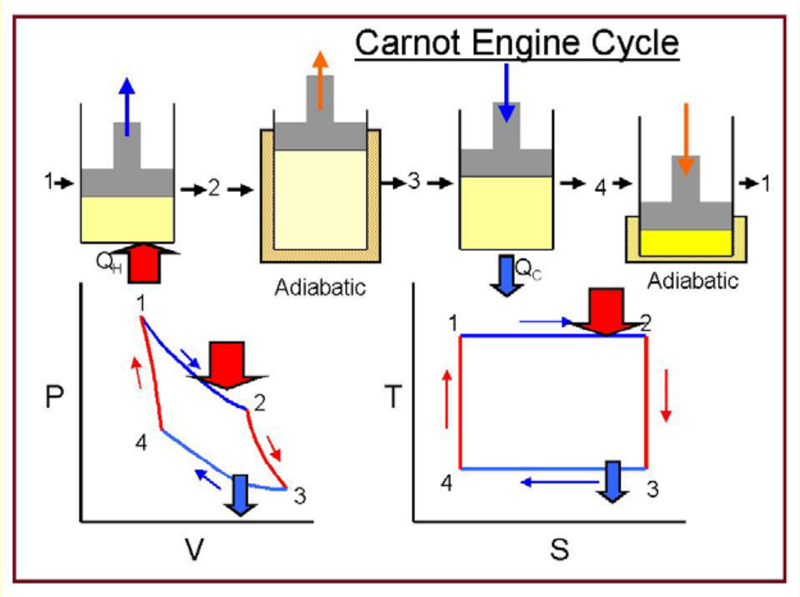
http://www.aip.org/history/gap/Gibbs/Gibbs.html

Gibbs' starting point for analyzing a system was the state of equilibrium, which is characterized by a maximum in the system's entropy.

Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium.

He proceeded to correct this situation, demonstrating for the first time the uses of the differential relationship in a system between energy E, pressure P, volume V, temperature T, and the entropy S, the last quantity then scarcely understood: $dE = TdS - PdV$.

http://www.aip.org/history/gap/Gibbs/Gibbs.html



http://www.colorado.edu/che/CLASSES/3320f/

Entropy Change during Carnot Cycle

1. Isothermal Expansion : $\Delta S = \Delta Q_{in}/T_{hot}$
2. Adiabatic Expansion : $\Delta S = 0$
3. Isothermal Compression: $\Delta S = -\Delta Q_{out}/T_{cold}$
4. Adiabatic Compression : $\Delta S = 0$

Since $\Delta Q_{in}/T_{hot} = \Delta Q_{out}/T_{cold}$,
$\Delta S_{total} = 0$

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

For a reversible case,

$$\Delta S = \frac{\Delta Q}{T} \quad \text{or} \quad dS = \frac{\delta Q}{T}$$

$\Delta E = T\Delta S - P\Delta V$

$dE = TdS - PdV$

→ a new form of the First and Second Laws

Enthalpy

$E + PV = \text{Enthalpy} = H$

$\Delta H = T\Delta S + V\Delta P$

$dH = TdS + VdP$

→ a new form of the First and Second Laws

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

$\Delta E = \Delta Q$ at constant volume

$\Delta Q = C_V \Delta T = \Delta E$

C_V : constant volume heat capacity

$$C_V = \frac{\Delta E}{\Delta T} \qquad \Delta E = \int_{T_1}^{T_2} C_v dT$$

$\Delta E = \Delta Q - \Delta W \qquad \Delta W = P\Delta V$

at constant pressure

$\Delta Q = \Delta E + P\Delta V = \Delta H$

$\Delta Q = C_P \Delta T = \Delta H$

C_P : constant pressure heat capacity

$$C_P = \frac{\Delta H}{\Delta T} \qquad \Delta H = \int_{T_1}^{T_2} C_p dT$$

Exercise Problem

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 the entropy produced 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

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

and the corresponding expression for solid lead is

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

Entropy change of the system

1. Step a → b: 1 most of supersaturated liquid lead is heated reversibly from 590 to 600 K at 1 atm pressure.

2. Step b → c: 1 mole of liquid lead is solidified reversibly at 600 K (The equilibrium melting or freezing temperature is the only temperature at which the melting or freezing process can be conducted reversibly).

3. Step c → d: 1 mole of solid lead is reversibly cooled from 600 to 590 K at 1 atm pressure.

As entropy is a state function,

$$\Delta S_{(a\to d)} = \Delta S_{(a\to b)} + \Delta S_{(b\to c)} + \Delta S_{(c\to d)}$$

$$\Delta S_{(a\to b)} = \int_a^b \frac{\delta Q_{rev}}{T} = \int_a^b \frac{\delta Q_p}{T} = \int_a^b \frac{nC_{p,Pb(l)}dT}{T}$$

$$= \int_{590K}^{600K} \frac{nC_{p,Pb(l)}dT}{T} = \int_{590K}^{600K}\left(\frac{32.4}{T} - 3.1\times10^{-3}\right)dT$$

$$= 32.4\,ln\frac{600}{590} - 3.1\times10^{-3}\times(600-590) = +0.514\ J/K$$

$$\Delta S_{(b\to c)} = \frac{Q_{rev}}{T} = \frac{Q_p}{T} = -\frac{4810}{600} = -8.017\ J/K$$

$$\Delta S_{(c\to d)} = \int_c^d \frac{\delta Q_{rev}}{T} = \int_c^d \frac{\delta Q_p}{T} = \int_{600K}^{590K} \frac{nC_{p,Pb(s)}dT}{T}$$

$$= \int_{600K}^{590K}\left(\frac{23.6}{T} + 9.75\times10^{-3}\right)dT$$

$$= 23.6\,ln\frac{590}{600} + 9.75\times10^{-3}\times(590-600) = -0.494\ J/K$$

$$\Delta S_{(a\to d)} = +0.514 - 8.017 - 0.494 = -7.997\ J/K$$

As the heat is transferred at constant temperature, then $Q_p = \Delta H$
As H is a state function,

$$\Delta H_{(a\to d)} = \Delta H_{(a\to b)} + \Delta H_{(b\to c)} + \Delta H_{(c\to d)}$$

$$\Delta H_{(a\to b)} = \int_a^b nC_{p,Pb(l)}dT = \int_{590K}^{600K}\left(32.4 - 3.1\times10^{-3}T\right)dT$$

$$= 32.4\times(600-590) - \frac{3.1\times10^{-3}}{2}(600^2 - 590^2) = +306\ J$$

$$\Delta H_{(b\to c)} = -4810\ J$$

$$\Delta H_{(c\to d)} = \int_{600K}^{590K} nC_{p,Pb(s)}dT = \int_{600K}^{590K}\left(23.6 + 9.75\times10^{-3}T\right)dT$$

$$= 23.6\times(590-600) + \frac{9.75\times10^{-3}}{2}(590^2 - 600^2) = -294\ J$$

$$\Delta H_{(a\to d)} = \Delta Q_p = -4799\ J \qquad \Delta S_{surrounding} = \frac{4799}{590} = 8.134\ J/K$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} = -7.994 + 8.134 = 0.137\ J/K$$

$$\Delta H_{(a\to d)} = \Delta Q_p = -4799\ J \qquad \Delta S_{surrounding} = \frac{4799}{590} = 8.134\ J/K$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} = -7.994 + 8.134 = 0.137\ J/K$$

$$\Delta G = ?$$

$$\Delta G = \Delta H_{(a\to d)} - T\Delta S_{(a\to d)}$$
$$= -4799\ J - 590 \times (-7.994J/k) = -82.54\ J$$

$$\Delta G = -T\Delta S_{total} = -590 \times 0.137 = -80.83J$$
$$= -T\left(\Delta S_{system} + \Delta S_{surrounding}\right) = -T\left(-7.994 + \frac{4799}{T}\right)$$
$$= -T\left(-7.994 + \frac{4799}{T}\right) = 7.994T - 4799 = -82.54$$

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

ΔG = ΔH – TΔS   and dG = - SdT + VdP
이 두 식은 어떻게 다른가?
이 두 식에서 G는 어떻게 다른가?

Homework Problems

1) dG = - SdT + VdP, 이식을 이용해서 앞의 문제에서의 비가역 반응의 구동력을 구하여라.

Why do we consider Free Energy (Gibbs, Helmholtz)?

Why the term “free” energy?

$$dS = d_eS + d_iS$$

여기에서 dS는 시스템의 엔트로피
이 값은 + 혹은 – 가 될 수 있다.
즉, irreversibility의 기준은 d_iS이지 dS가 아니다.

d_iS를 구하려면 System으로의
열 출입뿐 만 아니라
Surrounding 으로의 열 출입을
고려해주어야 한다.

$$dS_{total} = dS_{sys} + dS_{surr}$$

$$= d_eS + d_iS - d_eS = d_iS$$

매번 dS_{total}을 구하려면, surrounding의 엔트로피 변화를 알아야 하고, 그러려면, surrounding의 온도를 알아야 하고, 여러 가지로 불편하다.

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

$$dG = dE + PdV + VdP - TdS - SdT$$

$$= dQ - PdV + PdV + VdP$$

$$- Td_eS - Td_iS - SdT$$

$$= Td_eS - Td_eS - Td_iS \quad \text{at const. } T \,\&\, P$$

$$= -Td_iS \quad \text{at const. } T \,\&\, P$$

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