Thermodynamics of Materials

4th Lecture
2008. 3. 12 (Wed.)

James Prescott Joule (1818-1889)

1 calorie = 4.1868 joules

http://www.corrosion-doctors.org/Biographies/JouleBio.htm
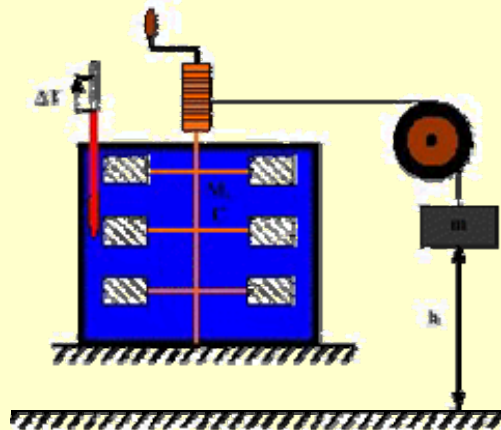
Mechanical Equivalent of Heat

Heat flow and **work** are both ways of transferring **energy**.
The **temperature** of a gas can be raised either by heating it,
by doing work on it, or a combination of the two.

In a classic experiment in 1843, James Joule showed the energy
equivalence of heating and doing work by using the change in
potential energy of falling masses to stir an insulated container
of water with paddles.

Careful measurements showed the increase
in the temperature of the water to be proportional to the
mechanical energy used to stir the water. At that time calories
were the accepted unit of heat and joules became the accepted
unit of mechanical energy

Interconvertibility of Heat and Work

1842 Mayer postulated the principle
       of conservation of energy.

1847 Helmholtz formulated the principle
       of conservation of energy,
   independent of Mayer.

1843-1848 Joule performed a series
             of experiments to establish
             the equivalence of work and heat.

Sir William Thomson, Lord Kelvin
(Belfast 1824 - Ayrshire 1907)

From Joule's claim that heat has the same potential for work, depending only on a temperature difference, Kelvin deduced that the efficiency of a Carnot engine is equal to

$$\frac{Work\ done}{Heat\ spent} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$
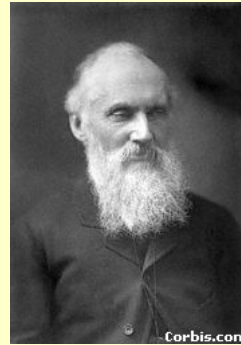
This conclusion allowed Lord Kelvin to derive the first rigorous definition of Absolute Temperature.

At zero K, all of the heat is converted into work at 100% efficiency.

Furthermore, Kelvin found that his "Absolute Zero" corresponds very closely to the temperature Gay-Lussac found as the zero volume point of an ideal gas. Absolute zero is – 273.15^{o}C.

Kelvin named the new science of heat and work "Thermodynamics".

Who did declare the First and Second Laws of Thermodynamics?

Rudolf Clausius (1822-1888)

Rudolf Clausius noticed the two expressions:

$$\Delta Q = C_V \Delta T \quad \text{at constant volume}$$

Heat added to increase temperature

$$J \Delta Q = P \Delta V \quad \text{at constant temperature}$$

Heat added to increase volume

$$\Delta Q = C_V \Delta T + L_T \Delta V$$

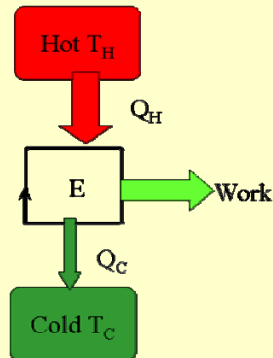Rudolf Clausius invented a quantity now called Internal Energy, U.

$$\Delta U = J \Delta Q - P \Delta V$$

$$\Delta U = \Delta Q - \Delta W$$

$\rightarrow$**The First Law**

Interconvertibility of heat and work

The Second Law is Carnot's assumption that work and heat cannot be created from nothing.

"Heat cannot itself pass from a cold body to a hotter body"

Kelvin's formulation of the efficiency of a reversible engine predicts that the maximum work an engine can do is given by this expression.

$$\Delta W = \Delta Q_{in} - \Delta Q_{out} = \Delta Q_{in}\left(\frac{\Delta Q_{in} - \Delta Q_{out}}{\Delta Q_{in}}\right)$$

$$= \Delta Q_{in}\frac{T_{hot} - T_{cold}}{T_{hot}}$$

$$\left(\Delta Q_{in} - \Delta Q_{out}\right)T_{hot} = \Delta Q_{in}\left(T_{hot} - T_{cold}\right)$$

$$\left(\Delta Q_{in} - \Delta Q_{out}\right)T_{hot} = \Delta Q_{in}\left(T_{hot} - T_{cold}\right)$$

$$\Delta Q_{in}T_{hot} - \Delta Q_{out}T_{hot} = \Delta Q_{in}T_{hot} - \Delta Q_{in}T_{cold}$$

$$\Delta Q_{out}T_{hot} = \Delta Q_{in}T_{cold} \rightarrow \frac{\Delta Q_{out}}{T_{cold}} = \frac{\Delta Q_{in}}{T_{hot}}$$

$$\rightarrow \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$\dfrac{\Delta Q}{T}$: *transformation equivalent*

If we allow heat to conduct freely between the two bodies,

$$\frac{\Delta Q}{T_{cold}} > \frac{\Delta Q}{T_{hot}}$$

But in a Carnot engine (reversible)

$$\frac{\Delta Q_{in}}{T_{hot}} = \frac{\Delta Q_{out}}{T_{cold}} \text{ : \textit{unchanged!}}$$

$$\frac{\Delta Q}{T} : \textit{transformation equivalent}$$

$$\frac{\Delta Q_{in}}{T_{hot}} = \frac{\Delta Q_{out}}{T_{cold}} : Entropy$$

$$\Delta S_{in} = \Delta S_{out}$$

$\therefore$ **Total entropy change for reversible process,**

$$\Delta S_{total} = \Delta S_{in} - \Delta S_{out} = 0$$

$$\frac{\Delta Q_{in}}{T_{hot}} = \frac{\Delta Q_{out}}{T_{cold}} = \Delta S \rightarrow \textit{for reversible process}$$

How can we estimate the total entropy change for the irreversible process, where we cannot define entropy?

$$\frac{\Delta Q}{T_{cold}} > \frac{\Delta Q}{T_{hot}}$$

$$\Delta S_{total} = \frac{\Delta Q}{T_{cold}} - \frac{\Delta Q}{T_{hot}} = \Delta Q \left(\frac{1}{T_{cold}} - \frac{1}{T_{hot}} \right)$$

$$= \Delta Q \left(\frac{T_{hot} - T_{cold}}{T_{cold} T_{hot}} \right) > 0$$

**When a stone falls on the ground,
the energy is conserved
at every moment of the process.**

**Then why doesn't the reverse process
occur?**

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*Previous thought on direction of a process
(irreversibility)*

- *A system containing more energy
  than another is less stable.
  (ex. Water flows downward.)*

- *Driving force for a process was
  exothermic enthalpy (ΔH).
  (ex. Supercooled water freezes.)*

All irreversible processes are accompanied by some heat generated by such as friction, which cannot be used.

$$Q' : \textit{Uncompensated Heat}$$

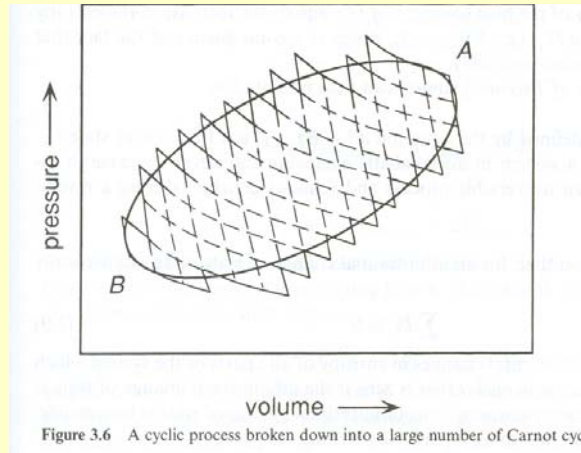$\rightarrow$ *Direction of Irreversibility!*

Then why don't we use Q' as a criterion for irreversibility or spontaneity?

$$\frac{\Delta Q}{T} : \textit{transformation equivalent}$$

$$\frac{\Delta Q_{in}}{T_{hot}} = \frac{\Delta Q_{out}}{T_{cold}} : \textit{Entropy}$$

If we allow heat to conduct freely between the two bodies,

$$\frac{\Delta Q}{T_{cold}} > \frac{\Delta Q}{T_{hot}}$$

Gaskell

Figure 3.6 A cyclic process broken down into a large number of Carnot cycl

$$\sum \frac{\Delta Q}{T} = 0 \qquad \therefore \oint \frac{\delta Q}{T} = 0 \qquad \frac{\Delta Q}{T} = S : state\ function$$

What is state function?

State variable and state function

- State variable : T, P, V, cf PV = nRT ; equation of state
- State function : E, H, F, G (energy)

함수 : 독립변수가 결정되면 종속변수가 하나 결정됨

상태함수 : 상태를 나타내는 변수, 즉, 압력, 온도, 부피 등을
          독립변수로 하는 함수

- state function : path independent
- path dependent한 함수를 배운 적이 있는가?

$$\oint dA = 0 \quad \rightarrow \quad \int_a^a dA = 0$$

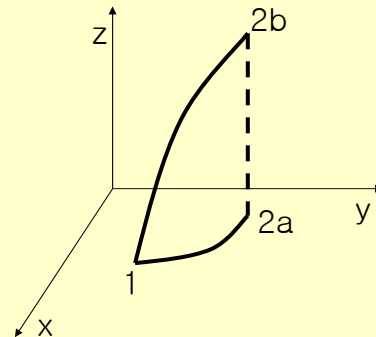$$\Delta f = f_2 - f_1 \qquad \Delta f(x) = f(x_2) - f(x_1)$$

$$\Delta f(x,y)_{1\rightarrow 2} = f(x_2, y_2) - f(x_1, y_1)$$

그러면 어떤 경우에 (상태)함수가 되지 않는가?
→ 주어진 독립변수로 함수 값이 하나로
   결정되지 않을 때

$$\Delta f(x,y,z)_{1\rightarrow 2} \neq f(x_2, y_2) - f(x_1, y_1)$$

state, x, y 에 대해서는 state function이 아니다.

그러나 state, x, y, z 에 대해서는 state function이다.

$[A(x,y)]_{2a} = [A(x,y)]_{2b}$
leads to $(\Delta A)_{\text{path } 1 \rightarrow 2a} = (\Delta A)_{\text{path } 1 \rightarrow 2b}$
whereas
$[B(x,y,z)]_{2a} \neq [B(x,y,z)]_{2b}$
leads to $(\Delta B)_{\text{path } 1 \rightarrow 2a} \neq (\Delta B)_{\text{path } 1 \rightarrow 2b}$

Work and Heat ≠ State Function

$$\delta w = PdV$$

To integrate this equation,
we must know how P depends upon on V.
However,

$$\frac{\delta w}{P} = dV$$

$$\int_1^2 \frac{\delta w}{P} = \int_1^2 dV = V_2 - V_1 = \Delta V$$

$$\rightarrow state\ function$$

$$\delta Q = dE + PdV$$

For ideal gas $PV = RT$

$$\delta Q = C_v dT + \frac{RT}{V} dV$$

Unless T is constant, the second term cannot be integrated.
We should know how T depends upon V.
However,

$$\frac{\delta Q}{T} = \frac{C_v dT}{T} + \frac{R}{V} dV$$

$$\int_1^2 \frac{\delta Q}{T} = C_v \, ln(T_2 / T_1) + R \, ln(V_2 / V_1)$$

$\rightarrow$ *state function*

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state ft이면 수학에서 확립된 성질을 이용할 수 있다.

Consider the function A(x,y)

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy$$

$\rightarrow$ Exact (Perfect, Total) Differentials

$$\left(\frac{\partial A}{\partial x}\right)_y = A에 \ 대한 \ x의 \ 편미분$$

$$\left(\frac{\partial A}{\partial y}\right)_x = A에 \ 대한 \ y의 \ 편미분$$

In this case, $\Delta A = A_2 - A_1$

$$dA = \left(\frac{\partial A}{\partial x}\right)_y dx + \left(\frac{\partial A}{\partial y}\right)_x dy \qquad \frac{\partial^2 A}{\partial x \partial y} = \frac{\partial^2 A}{\partial y \partial x}$$

$$dA = L(x, y)dx + M(x, y)dy$$

$$\left(\frac{\partial L}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

→ *Necessary and Sufficient Condition*
for Perfect Differentials (Euler reciprocity theorem)

$$\left(\frac{\partial L}{\partial y}\right)_x = \left(\frac{\partial M}{\partial x}\right)_y$$

: Euler's test for exact differentials
: Euler cross differentials
: Euler reciprocity theorem
When applied to thermodynamics,
this relation is called "Maxwell relation".

$$dE = \delta Q - \delta W = TdS - PdV$$
$$\rightarrow T = ? \qquad P = ?$$
$$\rightarrow \left(\frac{\partial T}{\partial V}\right)_S = ?$$

One of reasons that make thermodynamics look difficult
is that there are a numerous differential equations.

E : Internal Energy

$$dE = \delta Q - \delta W = TdS - PdV$$

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

$$\rightarrow T = \left(\frac{\partial E}{\partial S}\right)_V ; \quad P = -\left(\frac{\partial E}{\partial V}\right)_S \quad : \text{ Coefficient Relation}$$

$$\rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad : \text{ Maxwell Relation}$$

Conjugates of intensive and extensive variables
(T, S) (P, V)

Energy (or Work)
→ product of an intensive variable
and an extensive variable

$$T = \left(\frac{\partial E}{\partial S}\right)_V ; \quad P = -\left(\frac{\partial E}{\partial V}\right)_S \quad : \text{ Coefficient Relation}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad : \text{ Maxwell Relation}$$

Enthalpy=? $H = E + PV$ $dH = ?$

$$dH = dE + d(PV) = TdS + VdP$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$\rightarrow T = \left(\frac{\partial H}{\partial S}\right)_P \; ; \quad V = \left(\frac{\partial H}{\partial P}\right)_S \quad : Coefficient\ Relation$$

$$\rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad : Maxwell\ Relation$$

Helmholtz Free Energy=? $F = E - TS$

$dF = ?$ $dF = dE - d(TS) = -SdT - PdV$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \; ; \quad P = -\left(\frac{\partial F}{\partial V}\right)_T \; ; \; Coefficient\ Relation$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \; ; \; Maxwell\ Relation$$

$$\text{Gibbs Free Energy} = ? \qquad G = H - TS$$

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

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial T}\right)_P dT$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P ; \quad V = \left(\frac{\partial G}{\partial P}\right)_T ; \text{Coefficient Relation}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P ; \text{Maxwell Relation}$$

Conjugates for Non-PV Work

ϕ = potential difference
q = electric charge
(ϕ, q)

E = electric field
P = electric dipole moment
(E, P)

B = magnetic field
M = magnetic dipole moment
(B, M)

γ = interface energy
A = interface area
(γ, A)

$$dE = dQ + dW_{mech} + dE_q + dE_{elect} + dE_{mag} + dE_{interf}$$
$$= dQ - pdV + \phi\, dq - EdP - BdM + \gamma\, dA$$

Energy (or Work)
→ intensive variable x
differential of extensive variable
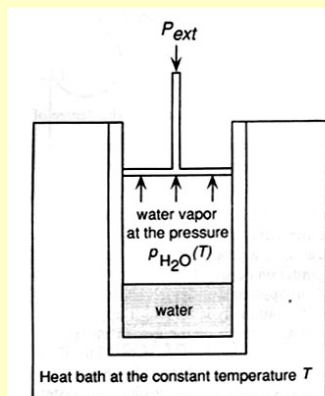
→ Thermodynamic Relation (Maxwell Relation)

Reversible and Irreversible Processes

Gaskell

Figure 3.2 A thermostatted piston and cylinder containing water and water vapor.

물과 포화된 수증기 시스템이 피스톤으로 외부 압력과
평형을 이루며 있다.
외부압력을 미세하게 줄이면 → $(P_{ext} - \Delta P)V$

다시 원위치 → $(P_{ext} + \Delta P)V$ 따라서 **permanent change** $2\Delta PV$
                          reversible process : $\Delta P = 0$

$$W_{max} = P_{ext}V \qquad Q_{rev} = \Delta E + W_{max}$$

따라서 $\quad Q_{rev} \succ Q_{irr}$

$$dS = \frac{\delta Q}{T}, (reversible)$$

$$dS \succ \frac{\delta Q}{T}, (irreversible)$$

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

Uncompensated heat Q'

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

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

$\delta Q' = 0, \quad reversible$
$\delta Q' \succ 0, \quad irreversible$

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

δQ : exchange with the outside world
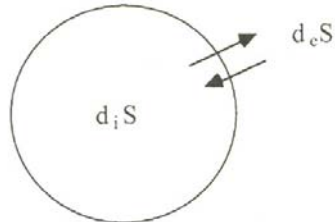$\delta Q'$: irreversible change
    in the interior of the system

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 = entropy production d_eS = entropy flow

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

$$dS = d_iS + d_eS$$

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

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

For open systems,

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