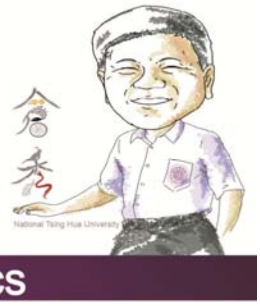
材 料 熱 力 學 一

Thermodynamics of Materials I



Chapter2 First Law of Thermodynamics

§ Energy convertion

- Frictionless: (1) kinetic E is conserved elastic collision
  (2) (K.E.) + (Potential E)=constant
  K.E. ⇔ P.E.
- Friction: K.E. ⇒ Thermal Energy

§ Relationship between Heat and Work

Joule's Experiments:

- adiabatically contained water
- Temp. increase $\propto$ work done
- different work employed:
  - (1) Rotating paddle wheel
  - (2) Compressing a cylinder of gas
  - (3) Rubbing two metal blocks
  - (4) electric motor driving a current through a coil
- "mechanical equivalent of heat"
- 1 cal (calorie, 15° calorie) ⇔ 1 gm water 14.5℃→15.5℃, heat required $1\ cal = \frac{1}{0.239}\ Joule = 4.184\ \ Joule$

§ The First Law of Thermodynamics

- Joule's experiments

(1) work done on water ⇒ Temp. increases
⇒ Internal Energy increases

$$\therefore \Delta U = U_B - U_A = -w \quad \begin{cases} \text{work done ``ON'' system, } W < 0 \\ \text{work done ``BY'' system, } W > 0 \end{cases}$$

(2) Temp. increase can be done by heating only

$$\Delta U = Q \quad \begin{cases} \text{heat “absorbed” by system, } Q > 0 \\ \text{heat “released” by system, } Q < 0 \end{cases}$$

$$\text{or} \quad \begin{cases} \text{endothermic} \quad Q > 0 \\ \text{exothermic} \quad Q < 0 \end{cases}$$

∴ First Law of Thermodynamics

"Energy conservation"

$$\begin{cases} \Delta U = Q - w \\ dU = \delta Q - \delta w \end{cases}$$

$$\begin{cases} \text{U: state function, indep. of path} \\ \text{Q, w: process function, dep. on path} \end{cases}$$

$$\begin{cases} \delta w_{\mathrm{Rev}} \equiv +PdV \\ w_{\mathrm{Rev}} = \int_1^2 PdV \end{cases}$$

$w_a > w_b > w_c$

$$\oint PdV \neq 0$$

$$\oint dU = 0$$

§ U is a state function, U=U(V,T)

$$\therefore dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

U=U(T,P) $\quad dU = \left(\frac{\partial U}{\partial P}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_P dT$

☆ Constant Volume Process (Isochore, isometric)

dV=0, ∴ $\delta w = 0$

$$dU_V = \delta Q_V, \quad \Delta U_V = Q_V$$

☆ Constant Pressure Process (Isobaric)

$$W_P = \int_1^2 PdV = P\int_1^2 dV = P(V_2 - V_1)$$

$\therefore U_2 - U_1 = Q_P - P(V_2 - V_1)$

$Q_P = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1$

define: $\boxed{H \equiv U + PV}$

$\therefore$constant P: $Q_P = \Delta H_P = H_2 - H_1$

§ Heat Capacity

$$C \equiv \frac{\delta Q_{rev}}{dT} \qquad \text{(J/K)}$$

constant volume: $C_v \equiv \left(\frac{\delta Q_{rev}}{dT}\right)_v$

constant pressure: $C_p \equiv \left(\frac{\delta Q_{rev}}{dT}\right)_p$

$$\therefore \quad C_v = \left(\frac{\delta Q}{dT}\right)_v = \left(\frac{dU}{dT}\right)_v \qquad \delta Q_v = dU_v = C_v dT$$

$$C_p = \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \qquad \delta Q_p = dH_p = C_p dT$$

* specific heat $s = \frac{C_p}{m}$

* molar heat capacity: c=C/n

☆ For any substance $C_p \geq C_v$ (one mole)

C_v: heat added is used to heat up only

C_p: heat added is used to { heat up; Expand system (work) }

* proof of $C_p > C_v$:

$$C_p \equiv \left(\frac{\delta Q}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p$$

$\because H \equiv U + PV$

$$\therefore C_p = \left(\frac{\partial U}{\partial T}\right)_p + \left[\frac{\partial (PV)}{dT}\right]_p$$

$$= \left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p$$

$$\therefore C_p - C_v = \left[\left(\frac{\partial U}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_p\right] - \left(\frac{\partial U}{\partial T}\right)_v \quad \ldots\ldots(1)$$

$$又\because dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\therefore \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_v \quad \ldots\ldots(2)$$

$$(2)\rightarrow(1) \quad C_p - C_v = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{C_p - C_v = \left(\frac{\partial V}{\partial T}\right)_p \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]} = \frac{TV\alpha^2}{\beta}$$

∗ note: (1) $P\left(\frac{\partial V}{\partial T}\right)_p$: work done "by" system to expand against external pressure

(2) $\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$: work done by system to expand against internal cohesive force acting between particles of substance

* For ideal gas, gas atoms (molecules) are not interacting ⇨ no internal cohesive form

$$\therefore \underline{\left(\frac{\partial U}{\partial V}\right)_T = 0}, \qquad \underline{C_p - C_v = R} \qquad \underline{C'_p - C'_v = nR}$$

$$\therefore C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P$$

one mole $PV = RT \quad V = \frac{RT}{P} \quad \therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$

$$\therefore C_p - C_v = P\frac{R}{P} = R$$

$$\begin{cases} \text{Ideal gas: } \left(\frac{\partial U}{\partial V}\right)_T = 0, \; U = U(T) \text{ only!!} \\ \text{Real gas: } \left(\frac{\partial U}{\partial V}\right)_T \to 0, \text{ very small } \left(\frac{\partial U}{\partial V}\right)_T \neq 0 \\ \text{Liquid and solids: } \left(\frac{\partial U}{\partial V}\right)_T \text{ is very large} \end{cases}$$

* Joule's experiment: ideal ($P_1 \rightarrow 0$)

Free expansion of ideal gas, adiabatically

Q=0, W=0, and observed $T \Rightarrow 0$

$$\therefore \Delta U = 0$$

$$\because dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT = 0 \quad \text{and} \quad dT=0,\ dV \neq 0$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$$

* Joule and Thomson: Real gas

dT≠0, $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$

§ Reversible, Adiabatic Process

* Reversible process: system passes infinitesimally through a continuum of equilibrium states

$$\delta W_{rev} = PdV$$

Adiabatic process: $\delta Q = 0$, $Q = 0$

$$\therefore dU = \delta Q - \delta w = -\delta w$$

one mole ideal gas:

state 1(T_1, V_1, P_1) $\xrightarrow{\text{Adia. Rev.}}$ state 2(T_2, V_2, P_2)

$$dU = C_v dT \qquad \delta W_{rev} = PdV$$

$$\therefore C_v dT = -PdV = -\frac{RT}{V}dV$$

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{C_v}\int_{V_1}^{V_2}\frac{dV}{V}$$

$$\therefore \ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_v}\ln\left(\frac{V_2}{V_1}\right) = \frac{R}{C_v}\ln\left(\frac{V_1}{V_2}\right) = \ln\left[\left(\frac{V_1}{V_2}\right)\frac{R}{C_v}\right]$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}}$$

one mole ideal gas: $C_p - C_v = R$, $\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$

令 $\gamma \equiv \left(\frac{C_p}{C_v}\right) > 1$ $\therefore \frac{R}{C_v} = \gamma - 1$ $\gamma = \frac{5}{3}$ monatomic ideal gas

$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}}$ $\therefore \boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}}$

又 $\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$ $\therefore \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$

$\therefore P_1V_1^{\gamma} = P_2V_2^{\gamma} = PV^{\gamma} = const$ reversible adiabatic ideal gas

§ Reversible, Isothermal processes (P_1, V_1, T)→(P_2, V_2, T)

* Isothermal process dT=0

$\because dU = \delta Q_{rev} - \delta w_{rev}$

ideal gas U=U(T) dT=0, dU=0

$\therefore \delta Q_{rev} = \delta w_{rev}$

$$Q_{rev} = w_{rev} = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \ln\left(\frac{V_2}{V_1}\right)$$

$$\therefore Q = w = RT \ln\left(\frac{V_2}{V_1}\right) = RT \ln\left(\frac{P_1}{P_2}\right)$$

c.p. Ideal gas $\begin{cases} \text{Reversible isothermal expansion} \\ \text{Reversible adiabatic expansion} \end{cases}$

P1→P2

$W_{isothermal} > W_{adiabatic}$

$\because \Delta U = Q - W$

Isothermal expansion: $\Delta U = 0$, $Q = W > 0$, 吸熱

Adiabatic expansion: $Q = 0 \quad \Delta U = -W < 0$，內能降低

Example: Monatomic ideal gas: ($C_v = \frac{3}{2}R \;\; C_p = \frac{5}{2}R \;\; \gamma = \frac{5}{3}$)

$$a \begin{cases} V_a = 10\ l \\ P_a = 10\ \text{atm} \\ T_a = 25℃ = 298\ \text{K} \end{cases} \qquad \begin{pmatrix} P_b = 1\ \text{atm} \\ T_b = 298\ \text{K} \end{pmatrix}$$

Q:
1. Reversible isothermal expansion b $\Delta U = ? \quad Q = ? \quad W = ? \quad \Delta H = ?$
2. Reversible adiabatic expansion c $\Delta U = ? \quad Q = ? \quad W = ? \quad \Delta H = ?$
3. ΔU is indep. of processes:

(1) (isothermal + isochore) a→e→c

(2) (isochore + isothermal) a→d→c

(3) (isothermal + isobaric) a→b→c

(4) (isochore + isobaric) a→f→c

(5) (isobaric + isochore) a→g→c

§ Sol:

1. $n = \frac{PV}{RT} = \frac{10 \times 10}{0.082 \times 298} = 4.09(moles)$

Isothermal: $T_b = T_a = 298$ K

$\because P_b V_b = P_a V_a = nRT_a \quad V_b = \frac{P_a V_a}{P_b} = 100\ liters$

$U = U(T) \qquad \Delta U = 0$

$$Q = W = \int_a^b PdV = \int_a^b \frac{nRT}{V} dV = nRT \ln\left(\frac{V_b}{V_a}\right) = 23.3(KJ)$$

$$C_p = \left(\frac{dH}{dT}\right)_P \qquad dH = dH_P = C_p dT$$

$$0 = \int_a^b nC_p dT = \Delta H = H_b - H_a = (U_b + P_b V_b) - (U_a + P_a V_a) = 0$$

2. Adiabatic: Q=0 $\quad P_c = 1$ atm

$$P_a V_a^{\gamma} = P_c V_c^{\gamma} \qquad \gamma = \frac{C_p}{C_v} = \frac{5/2R}{3/2R} = \frac{5}{3}$$

$$\therefore V_c = \left(\frac{P_a V_a^{\gamma}}{P_c}\right)^{\frac{1}{\gamma}} = \left(\frac{10\times 10^{\frac{5}{3}}}{1}\right)^{\frac{3}{5}} = 39.8 \ liter$$

$$T_c = \frac{P_c V_c}{nR} = \frac{1\times 39.8}{4.09\times 0.082} = 119(K)$$

$$\Delta U = \int_a^c nC_v dT = nC_v(T_c - T_a) = -9.13(KJ) = -W$$

$$\Delta H = \int_a^c nC_p dT = nC_p(T_c - T_a) = -15.2(KJ)$$

$$P_a V_a^{\gamma} = const = 10\times 10^{\frac{5}{3}} = 14.39$$

$$W = \int_{V_a}^{V_c} PdV = \int \frac{const}{V^{\gamma}} dV = const \times \frac{1}{1-\gamma}\left[V_c^{1-\gamma} - V_a^{1-\gamma}\right] = 9.13(KJ)$$

3. (1) $a \xrightarrow{dT=0} e \xrightarrow{dV=0} c$

a→e, $dT=0$, $\triangle U_{ae}=0$ $T_a=T_e$

e→c, $dV=0$, $\Delta U_{ec} = \int_e^c nC_v dT = nC_v(T_c - T_e) = nC_v(T_e - T_a) = -9.13 \ KJ$

$\therefore \Delta U_{(1)} = -9.13 \ KJ$

(2) a→d, $dV=0$ $\Delta U_{ad} = nC_v(T_d - T_a) = nC_v(T_c - T_a) = -9.13 \ KJ$

d→c, $T_d=T_c$ $dT=0$ $\Delta U_{dc} = 0$

$\therefore \Delta U_{(2)} = -9.13 \ KJ$

(3) a→b, $dT=0$ $\Delta U_{ab} = 0$

b→c, $dP=0$ $\Delta U_{bc} = \int_b^c nC_v dT = nC_v(T_c - T_b) = -9.13 \ KJ$

$\therefore \Delta U_{(3)} = -9.13 \ KJ$

(4) a→f, $dV=0$ $\Delta U = \int_a^f nC_v dT = nC_v(T_f - T_a) = -13.67 \ KJ$

f→c, $dP=0$ $\Delta U = \int_f^c nC_v dT = nC_v(T_c - T_f) = +4.54 \ KJ$

$\therefore \Delta U_{(4)} = -9.13 \ KJ$

(5) a→g, dP=0 $\Delta U = \int_a^g nC_v dT = nC_v \left(T_g - T_a\right) = +45.29\ \ KJ$

g→c, dV=0 $\Delta U = \int_g^c nC_v dT = nC_v \left(T_c - T_g\right) = -54.42\ \ KJ$

$\therefore \Delta U_{(5)} = -9.13\ \ KJ$

$\Delta U_{(1)} = \Delta U_{(2)} = \Delta U_{(3)} = \Delta U_{(4)} = \Delta U_{(5)} = \Delta U_2$ indep. of path