$$\therefore C_p - C_v = \left(\frac{\partial U}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_p + p \cdot \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p - C_v = \left[\underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{?} + \underbrace{p}_{\text{pressure}}\right] \times \left(\frac{\partial V}{\partial T}\right)_p = \boxed{\left(\frac{\alpha^2 T \cdot V}{\beta}\right)}$$

$p \cdot \left(\frac{\partial V}{\partial T}\right)_p$: work done against "external" pressure

$\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$: " " "internal" force

cohesion

* **Ideal Gas**

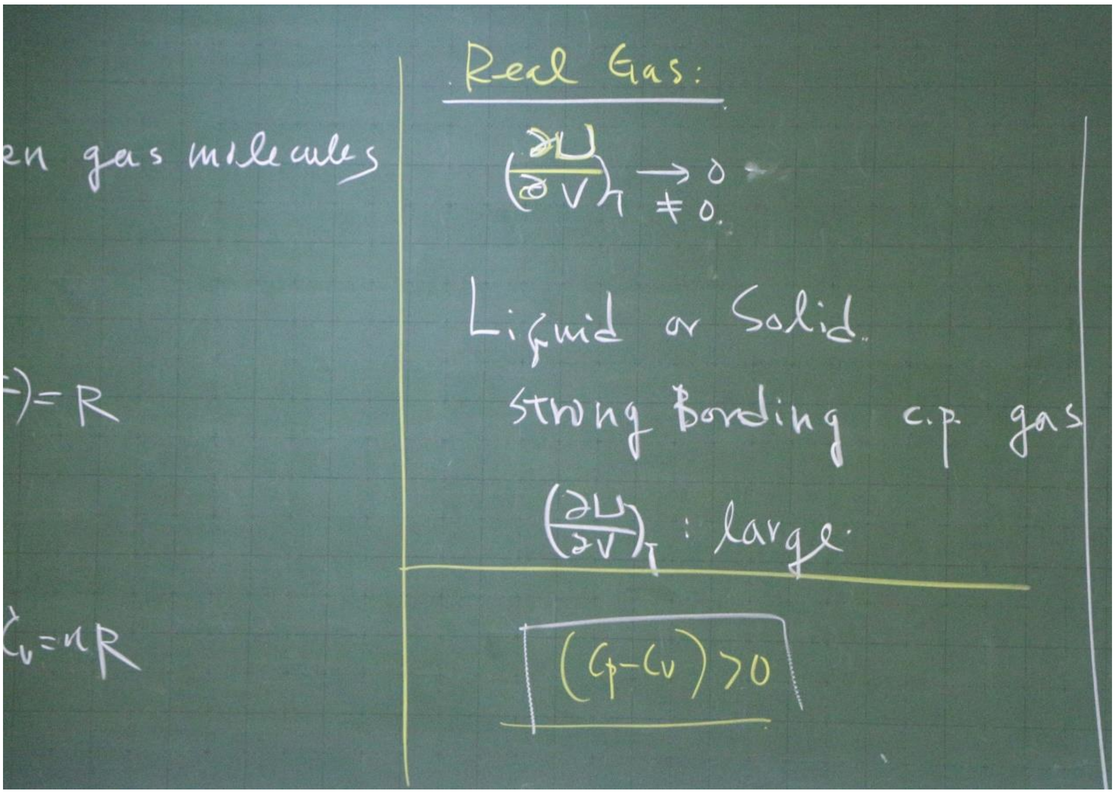
No interaction between gas molecules

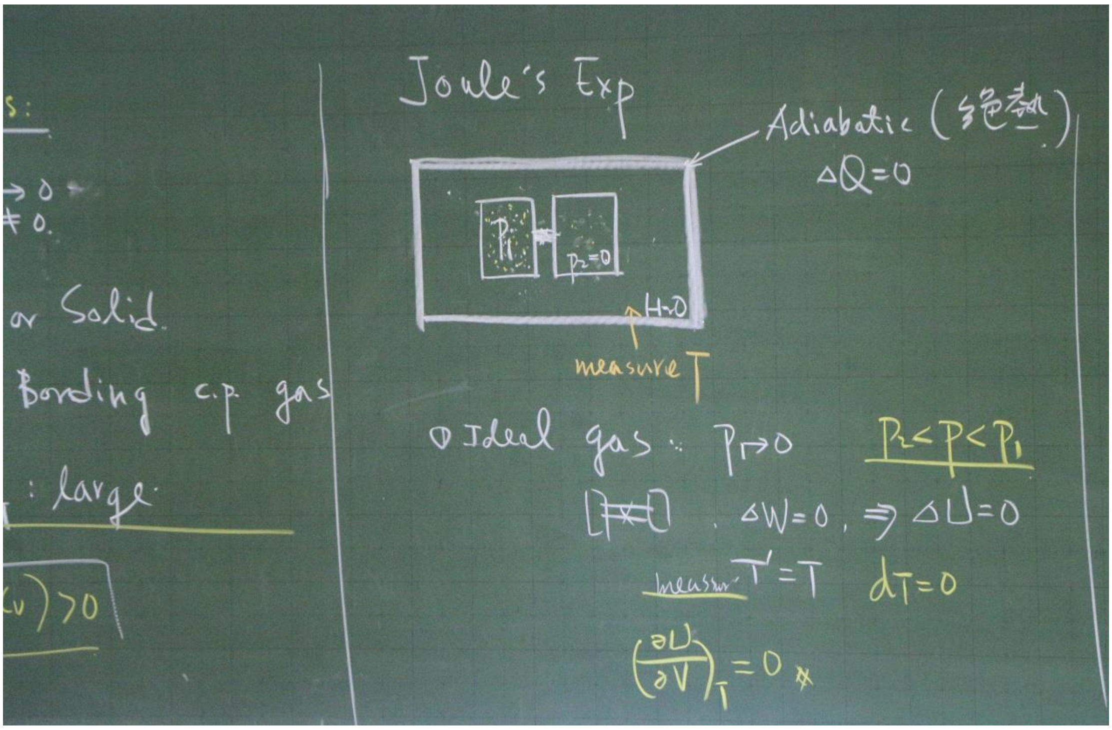
$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0} \#$$

$$C_p - C_v = p \cdot \left(\frac{\partial V}{\partial T}\right)_p = p \times \left(\frac{R}{p}\right) = R$$

$$pV = 1 \cdot RT \quad , \quad V = \frac{RT}{p}$$

$$\boxed{C_p - C_v = R} \# \qquad C_p - C_v = nR$$


en gas molecules
$)= R$
$C_v = nR$
Real Gas:
$\left(\frac{\partial U}{\partial V}\right)_T \to 0$
$\neq 0.$
Liquid or Solid.
strong Bonding c.p. gas
$\left(\frac{\partial U}{\partial V}\right)_T$: large.
$(C_p - C_v) > 0$


Joule's Exp
Adiabatic (绝热)
$\Delta Q = 0$
P_1
$P_2 = 0$
H_2O
measure T
① Ideal gas: $P_1 \to 0$
$P_2 < P < P_1$
$\Delta W = 0, \Rightarrow \Delta U = 0$
measure $T' = T$
$dT = 0$
$\left(\frac{\partial U}{\partial V}\right)_T = 0$

ic (绝热)

0

② Real Gas. $P_1 \gg P_2 = 0$

$dT \neq 0$ (very small)

$\left(\frac{\partial U}{\partial V}\right)_T \neq 0 \longrightarrow 0$

Ideal Gas: $C_p - C_v = R$

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

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

$U = U(T)$ indep. of P, V

$P_2 < P < P_1$

$\Delta U = 0$

$T = 0$

Adiabatic (绝热)

$\Delta Q = 0$

$P_f \to 0$

$P_2 < P < P_1$

$\Delta W = 0, \Rightarrow \Delta U = 0$

$T' = T \quad dT = 0$

$= 0$ ☆

② Real Gas. $P_1 \gg P_2 = 0$

$dT \neq 0$ (very small)

$\left(\frac{\partial U}{\partial V}\right)_T \neq 0 \longrightarrow 0$

Ideal Gas: $C_p - C_v = R$

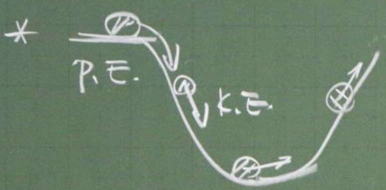
$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$

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

$U = U(T)$ indep. of P, V

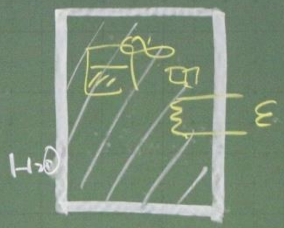
Ch.2 1st Law

§ Energy Convertion.

* 

§ Work $\rightleftarrows$ $\boxed{\text{Heat}}$?

Joule's Exp



Work → $\boxed{\text{Heat}}$?

unit? calorie (cal) T.

$\boxed{1\ cal}$ ⇔ 1 gm H_2O (water)

15° 14.5°C → 15.5°C

1 cal = 4.184 J (N-m)

H2O

"System"

N" system

…ic)

…ic)

能量守恆

☆ 1st Law: energy conservation

$$\boxed{\Delta U = \Delta Q - \Delta W}$$

or

$$\boxed{dU = \delta Q - \delta W}$$

$$\Delta Z = \int_1^2 dZ$$

rev: (可逆) Reversible

$\boxed{\text{Work}}$?

Force

$$\delta W \equiv \vec{F} \cdot d\vec{z}$$

⇕

$$\boxed{\delta W_{rev} \equiv P \cdot dV}$$

Mechanical Work.

Force

F

P

能量守恆

Energy conservation

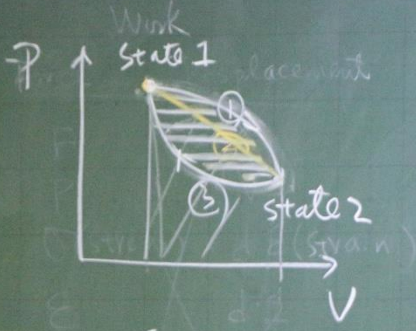
$\boxed{\Delta W}$ ✓

$\boxed{\oint \delta W}$ ✓

rev: (可逆)

Reversible

Mechanical Work. ✓



$\Delta W_{①} = \int_{①} p \cdot dV$

$\Delta W_{①} \neq \Delta W_{②} \neq \Delta W_{③}$ ΔQ

$\oint \delta W \overset{?}{\neq} 0$. $\oint \delta Q \overset{?}{\neq} 0$

$\oint dU = 0$ U: state function

§ U: state function

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

$U = U(T, p) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$

* Constant Volume (fixed V)

$dV = 0$. $\delta W_{rev} = 0$ ∴ $\Delta W = 0$

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

* Constant Pressure (fixed p)

$\Delta W_p = \int_1^2 p \cdot dV = p \int_1^2 dV = p(V_2 - V_1)$

$\Delta U_p = \Delta Q_p - \Delta W_p$

$(U_2 - U_1) = \Delta Q_p - p(V_2 - V_1)$

state 2

(strain)

V

ΔQ

$\oint \delta Q \overset{?}{\neq} 0$

U: state function

§ U: state function

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

$$U = U(T,p) \Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_p dT + \left(\frac{\partial U}{\partial p}\right)_T dp$$

* Constant Volume (fixed V)

$$dV = 0 \quad \delta W_{rev} = 0 \;\therefore\; \Delta W = 0$$

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

* Constant Pressure (fixed p)

$$\Delta W_p = \int_1^2 p\cdot dV = p\int_1^2 dV = p(V_2 - V_1)$$

$$\Delta U_p = \Delta Q_p - \Delta W_p$$

$$(U_2 - U_1) = \Delta Q_p - p(V_2 - V_1)$$

$$\Delta Q_p = (U_2 - U_1) + p(V_2 - V_1)$$

$$= (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1$$

If $\boxed{H \equiv U + p\cdot V}$ ☆

enthalpy (焓)

$$\therefore \Delta Q_p = \Delta H_p$$

$$\boxed{\delta Q_p = dH_p}$$

$p(V_2 - V_1)$

$(U_1 + pV_1) = H_2 - H_1$

$\boxed{p \cdot V}$ ☆

§ Heat Capacity

☆ $$\boxed{C \equiv \left(\frac{\delta Q}{dT}\right)}$$

$$c = \frac{C}{n} \quad \left(\frac{J}{mole \cdot °C}\right)$$

Specific Heat : $s = \frac{C}{m}$ $\left(\frac{J}{gm\,°C}\right)$

C_p
C_v c.p.

Heat Capacity

$$C \equiv \left(\frac{\delta Q}{dT}\right)$$

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

$\delta Q_V = dU_V$ | $C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$

$\boxed{C_p > C_V}$? proof

$(C_p - C_V) > 0$

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

$\because$ $\delta Q_p = dH_p$, $\boxed{H \equiv U + p \cdot V}$

$\therefore$ $C_p = \left(\frac{\partial U}{\partial T}\right)_p + p \cdot \left(\frac{\partial V}{\partial T}\right)_p$

$\therefore$ $C_p - C_V = \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] - \left(\frac{\partial U}{\partial T}\right)_V$

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

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

Heat Capacity

$$C \equiv \left(\frac{\delta Q}{dT}\right)$$

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

$\delta Q_V = dU_V$

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$\boxed{C_p > C_V}$? proof

$(C_p - C_V) > 0$

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

$\because \delta Q_p = dH_p$, $\boxed{H \equiv U + p \cdot V}$

$$\therefore C_p = \left(\frac{\partial U}{\partial T}\right)_p + p \cdot \left(\frac{\partial V}{\partial T}\right)_p$$

$$\therefore C_p - C_V = \left[\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] - \left(\frac{\partial U}{\partial T}\right)_V$$

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

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