

Chapter 5: Part B

Simple applications of macroscopic thermodynamics

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- Important relationships between macroscopic quantities
- Based on the fundamental thermodynamic laws (0th, 1st, 2nd, 3rd)
- Quantities such as p , E always are mean values

Independent variables:

- Most of systems only have the external parameters V ;
- two independent variables can specify the system, such as E and V ; or E and P ; or T and V ... Other variables can be determined by the two independent variables;

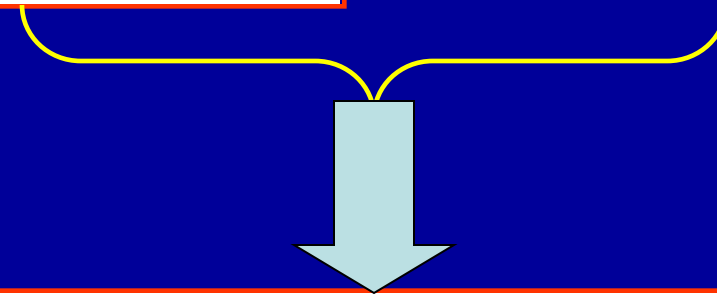
Fundamental equations:

1st law

$$dQ = dE + dW$$

2nd law

$$dQ = T dS$$



$$T dS = dE + p dV$$

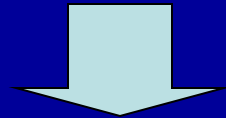
Properties of ideal gas

5.1 Equation of state and internal energy



$$pV = \nu RT$$

$$\begin{aligned}\Omega &\propto V^N \chi(E) \\ \beta &= \frac{\partial \ln \chi(E)}{\partial E} \\ \beta &= \beta(E)\end{aligned}$$



$$E = E(T) \quad \text{independent of } V$$

General relations for a homogeneous substance

5.6 Summary of Maxwell relations and thermodynamic functions

Maxwell relations

$$dE = T dS - p dV$$

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial p}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_p \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial p}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_p\end{aligned}$$

*T, p, V, S are not
completely in-dependent*

???

One can use Ω to give a complete macroscopic description on system

General relations for a homogeneous substance

5.6 Summary of Maxwell relations and thermodynamic functions

Maxwell relations

??? One can use Ω to give a complete macroscopic description on system

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_V \quad \text{and} \quad p = T \left(\frac{\partial S}{\partial V} \right)_E$$

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_V dE + \left(\frac{\partial S}{\partial V} \right)_E dV \\ &= \frac{1}{T} dE + \frac{p}{T} dV \quad \text{by (5.6.6)} \end{aligned}$$

(T, S)

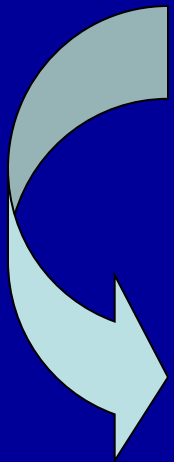
and

(p, V)

Number of states

generalized force

General relations for a homogeneous substance thermodynamic functions



| | |
|------------------------|---------------|
| E | $E = E(S, V)$ |
| $H \equiv E + pV$ | $H = H(S, p)$ |
| $F \equiv E - TS$ | $F = F(T, V)$ |
| $G \equiv E - TS + pV$ | $G = G(T, p)$ |

| |
|---------------------|
| $dE = T dS - p dV$ |
| $dH = T dS + V dp$ |
| $dF = -S dT - p dV$ |
| $dG = -S dT + V dp$ |

General relations for a homogeneous substance


5.7 Specific heats

at constant volume

$$C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

at constant pressure

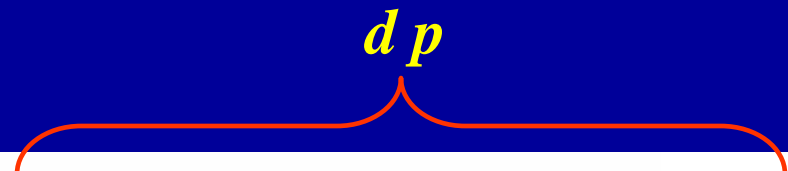
$$C_p = \left(\frac{dQ}{dT} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$


$$dQ = T dS = T \left[\left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \right]$$

$$dQ = T dS = C_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

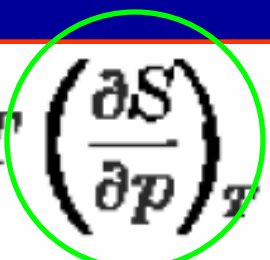
General relations for a homogeneous substance

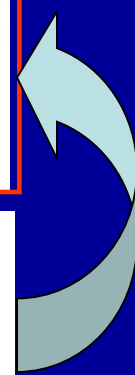
5.7 Specific heats

$$dQ = T dS = C_p dT + T \left(\frac{\partial S}{\partial p} \right)_T \left[\left(\frac{\partial p}{\partial T} \right)_V dT + \left(\frac{\partial p}{\partial V} \right)_T dV \right]$$


when V is constant

$$dQ = C_V dT$$

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V$$


$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p$$


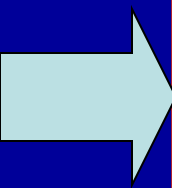
The quantities in the right of equation is easily to be measured

General relations for a homogeneous substance

5.7 Specific heats

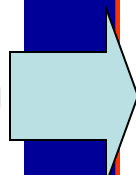
$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

volume coefficient of expansion


$$\left(\frac{\partial S}{\partial p} \right)_T = -V\alpha$$

constant volume

$$dV = \left(\frac{\partial V}{\partial T} \right)_p dT + \left(\frac{\partial V}{\partial p} \right)_T dp$$


$$\left(\frac{\partial p}{\partial T} \right)_V = - \frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T}$$

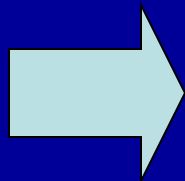
General relations for a homogeneous substance

5.7 Specific heats

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V = C_p + T \left(\frac{\partial S}{\partial p} \right)_T \left(\frac{\partial p}{\partial T} \right)_V$$

$$\kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

isothermal compressibility



$$\left(\frac{\partial p}{\partial T} \right)_V = \frac{\alpha}{\kappa}$$

$$C_V = C_p + T(-V\alpha) \left(\frac{\alpha}{\kappa} \right)$$

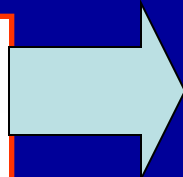
$$C_p - C_V = VT \frac{\alpha^2}{\kappa}$$

General relations for a homogeneous substance

5.7 Specific heats: example---ideal gas

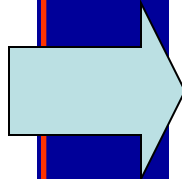
For ideal gas:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$



$$\begin{aligned} p dV &= \nu R dT \\ \left(\frac{\partial V}{\partial T} \right)_P &= \frac{\nu R}{p} \\ \alpha &= \frac{1}{V} \left(\frac{\nu R}{p} \right) = \frac{\nu R}{\nu R T} = \frac{1}{T} \end{aligned}$$

$$\kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$



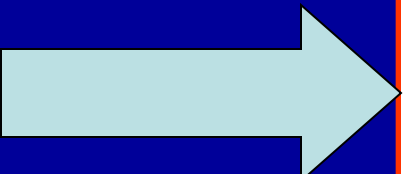
$$\begin{aligned} p dV + V dp &= 0 \\ \left(\frac{\partial V}{\partial p} \right)_T &= - \frac{V}{p} \\ \kappa &= - \frac{1}{V} \left(- \frac{V}{p} \right) = \frac{1}{p} \end{aligned}$$

General relations for a homogeneous substance

5.7 Specific heats: example---ideal gas

For ideal gas:

$$C_p - C_v = VT \frac{\alpha^2}{\kappa}$$


$$C_p - C_v = VT \frac{(1/T)^2}{1/p} = \frac{Vp}{T} = \nu R$$


$$c_p - c_v = R$$

General relations for a homogeneous substance

5.7 Specific heats

Limiting properties near absolute zero

3rd law

$$\text{as } T \rightarrow 0, \quad S \rightarrow S_0$$

$$\partial S / \partial T \approx \text{finite value}$$

In differential form

$$\text{as } T \rightarrow 0$$

$$C_V = \left(\frac{\partial Q}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V \rightarrow 0$$

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P \rightarrow 0$$

General relations for a homogeneous substance

5.7 Specific heats

Limiting properties near absolute zero

In integration form

$$S(T) - S(0) = \int_0^T \frac{C_V(T')}{T'} dT'$$

finite value

Guarantee converge

$$\text{as } T \rightarrow 0, \quad C_V(T) \rightarrow 0$$

Maxwell relation

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) = \frac{1}{V} \left(\frac{\partial S}{\partial p} \right) = 0$$

General relations for a homogeneous substance

5.7 Specific heats

Limiting properties near absolute zero

$$\kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

Remains finite value in ground state

$$C_p - C_v = VT^2 \frac{\alpha^2}{\kappa}$$

Decrease to 0 very rapidly

$$\text{as } T \rightarrow 0,$$

$$\frac{C_p - C_v}{C_v} \rightarrow 0$$

General relations for a homogeneous substance

5.7 Specific heats

Limiting properties near absolute zero

How about ideal gas?

$$c_p - c_v = R$$

$T \rightarrow 0$, system approaches the ground state, quantum mechanic effects will become important, and the classic equation of $pV = \nu RT$ will become invalid.

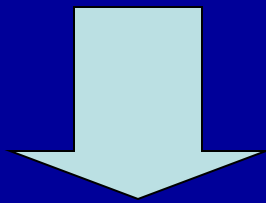
General relations for a homogeneous substance

5.8 Entropy and internal energy

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$S = S(T, V)$$
$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

$$\left(\frac{\partial S}{\partial T} \right)_V = \frac{1}{T} C_V$$
$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$$



$$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV$$

?



Equation of state

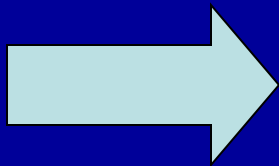
General relations for a homogeneous substance

5.8 Entropy and internal energy

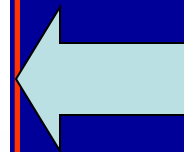
$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

$$\left(\frac{\partial C_V}{\partial V} \right)_T = \left(\frac{\partial}{\partial V} \right)_T \left[T \left(\frac{\partial S}{\partial T} \right)_V \right]$$

$$\begin{aligned} &= T \frac{\partial^2 S}{\partial T \partial V} = T \left(\frac{\partial}{\partial T} \right)_V \left(\frac{\partial S}{\partial V} \right)_T \\ &= T \left(\frac{\partial}{\partial T} \right)_V \left(\frac{\partial p}{\partial T} \right)_V \end{aligned}$$



$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_V$$



**Equation
of state**

General relations for a homogeneous substance

5.8 Entropy and internal energy

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_V$$

All the thermodynamic properties can be evaluated by the entropy!

1, heat capacity as a function of T at $V=V_1$

2, equation of state

$$C_V(T, V) = C_V(T, V_1) + \int_{V_1}^V \left(\frac{\partial C_V(T, V')}{\partial V}\right)_T dV' \quad \rightarrow C_V$$

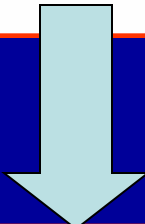
$$S(T, V) - S(T_0, V_0) = [S(T, V) - S(T_0, V)] + [S(T_0, V) - S(T_0, V_0)]$$

$$\int dT$$

$$\int dV$$

General relations for a homogeneous substance

5.8 Entropy and internal energy

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV$$


$$S(T, V) - S(T_0, V_0) = \int_{T_0}^T \frac{C_V(T', V)}{T'} dT' + \int_{V_0}^V \left(\frac{\partial p(T_0, V')}{\partial T} \right)_V dV'$$

General relations for a homogeneous substance

5.8 Entropy and internal energy

$$dE = T dS - p dV$$

Fundamental equation

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial p}{\partial T} \right)_v dV$$

$$dE = C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dV$$

$$dE = \left(\frac{\partial E}{\partial T} \right)_v dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

$$\begin{aligned} \left(\frac{\partial E}{\partial T} \right)_v &= C_v \\ \left(\frac{\partial E}{\partial V} \right)_T &= T \left(\frac{\partial p}{\partial T} \right)_v - p \end{aligned}$$

General relations for a homogeneous substance

5.8 Entropy and internal energy: example

Van de Waals gas

Equation of state

$$pv = RT$$

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Additional positive pressure and occupied volume

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$
$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}$$

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p = \frac{RT}{v - b} - p$$

$$\left(\frac{\partial \epsilon}{\partial v}\right)_T = \frac{a}{v^2}$$

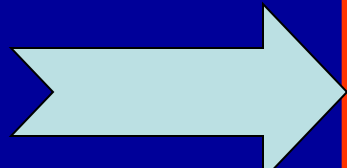
General relations for a homogeneous substance

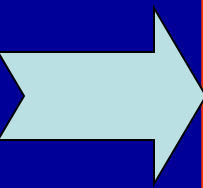
5.8 Entropy and internal energy: example

Van de Waals gas

$$\left(\frac{\partial c_V}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right) = T \left(\frac{\partial}{\partial T}\right)_v \left(\frac{R}{v-b}\right) = 0$$


$$c_V = c_V(T)$$


$$d\epsilon = c_V(T) dT + \frac{a}{v^2} dv$$


$$\begin{aligned}\epsilon(T, v) - \epsilon(T_0, v_0) &= \int_{T_0}^T c_V(T') dT' - a \left(\frac{1}{v} - \frac{1}{v_0}\right) \\ \epsilon(T, v) &= \int_{T_0}^T c_V(T') dT' - \frac{a}{v} + \text{constant}\end{aligned}$$

General relations for a homogeneous substance

5.8 Entropy and internal energy: example Van de Waals gas

If c_V is independent of temperature,

$$e(T,v) = c_V T - \frac{a}{v} + \text{constant}$$

$$ds = \frac{c_V(T)}{T} dT + \frac{R}{v-b} dv$$

$$s(T,v) - s(T_0,v_0) = \int_{T_0}^T \frac{c_V(T')}{T'} dT' + R \ln \left(\frac{v-b}{v_0-b} \right)$$

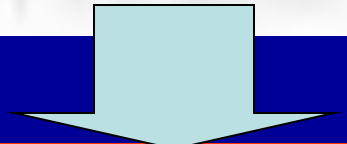
If c_V is independent of temperature,

$$s(T,v) = c_V \ln T + R \ln (v-b) + \text{constant}$$

General relations for a homogeneous substance

5.8 Entropy and internal energy: example

Van de Waals gas

$$ds = \frac{c_v(T)}{T} dT + \frac{R}{v-b} dv$$


$$s(T,v) - s(T_0,v_0) = \int_{T_0}^T \frac{c_v(T')}{T'} dT' + R \ln \left(\frac{v-b}{v_0-b} \right)$$

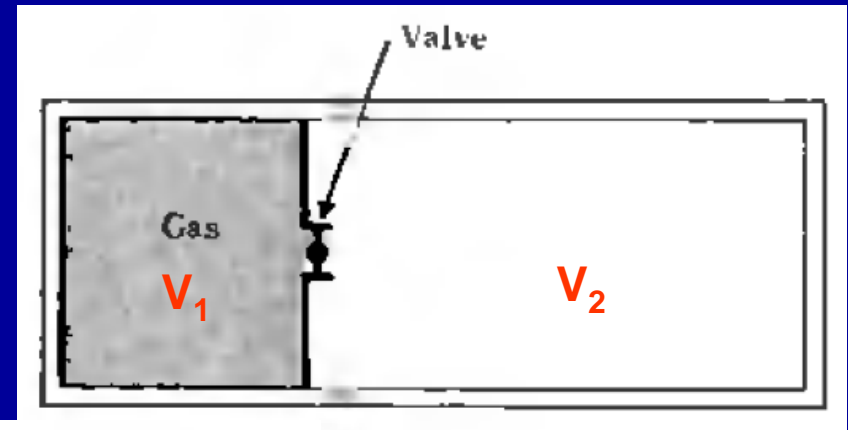
If c_v is independent of temperature,

$$s(T,v) = c_v \ln T + R \ln (v-b) + \text{constant}$$

Free energy expansion and throttling process

5.9 free expansion

Open valve and the gas is free to expand to fill the volume V_2 from V_1



container is adiabatically insulated,

$$Q = 0$$

does no work in the process

$$W = 0$$

First law



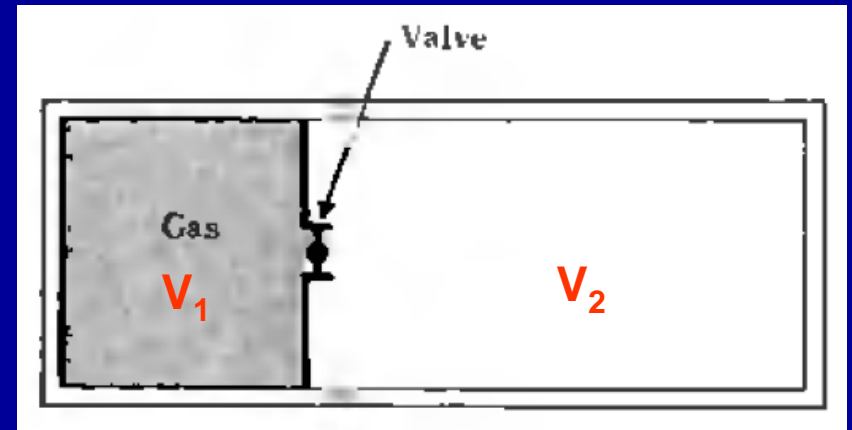
$$\Delta E = 0$$

Free energy expansion and throttling process

5.9 free expansion

First law

$$\Delta E = 0$$



Then

$$E(T_2, V_2) = E(T_1, V_1)$$

Specially, for ideal gas

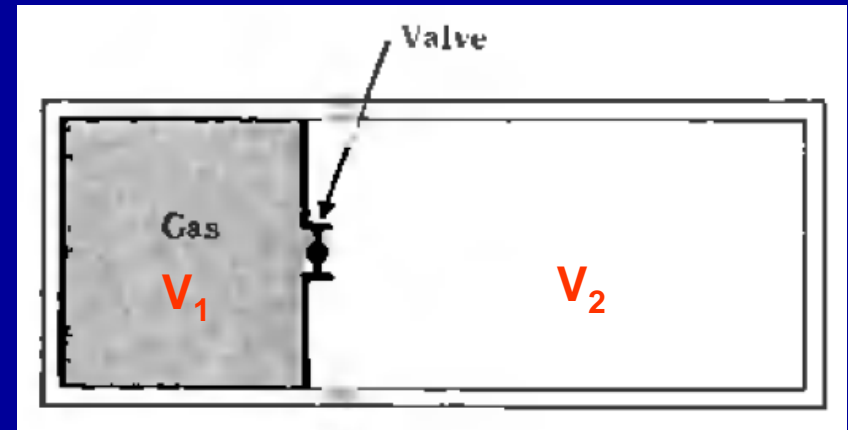
$$E(T_2) = E(T_1)$$

Generally,

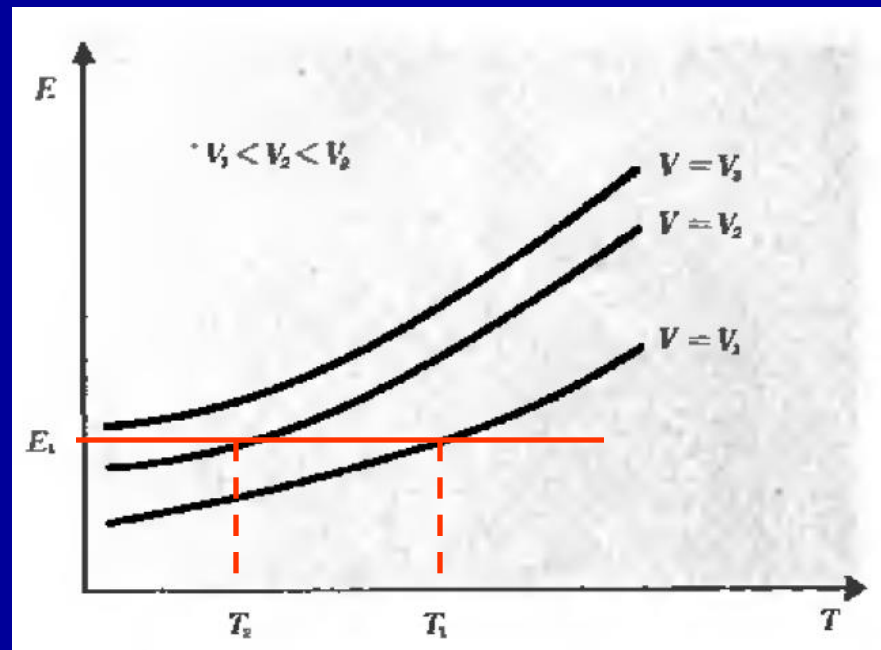
$$E(T_2, V_2) = E(T_1, V_1)$$

Free energy expansion and throttling process

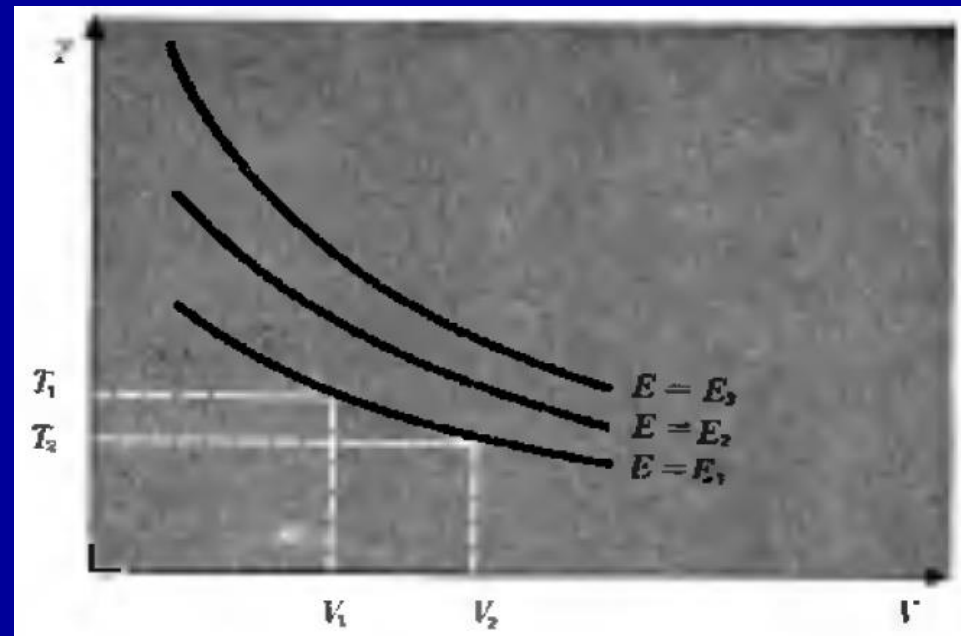
5.9 free expansion



E-T curve



V-T curve

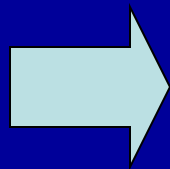


Free energy expansion and throttling process

5.9 free expansion: example

Van de Waals gas

$$\epsilon(T_2, v_2) = \epsilon(T_1, v_1)$$



$$\int_{T_1}^{T_2} c_V(T') dT' - \frac{a}{v_2} = \int_{T_1}^{T_2} c_V(T') dT' - \frac{a}{v_1}$$

$$\int_{T_1}^{T_2} c_V(T') dT' - \int_{T_0}^{T_1} c_V(T') dT' = a \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

$$\int_{T_1}^{T_2} c_V(T') dT' = a \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

Free energy expansion and throttling process

5.9 free expansion: example

$$\epsilon(T_2, v_2) = \epsilon(T_1, v_1)$$

Van de Waals gas

Ignore c_v change in $[T_1, T_2]$

$$c_v(T_2 - T_1) = a \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$
$$T_2 - T_1 = -\frac{a}{c_v} \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

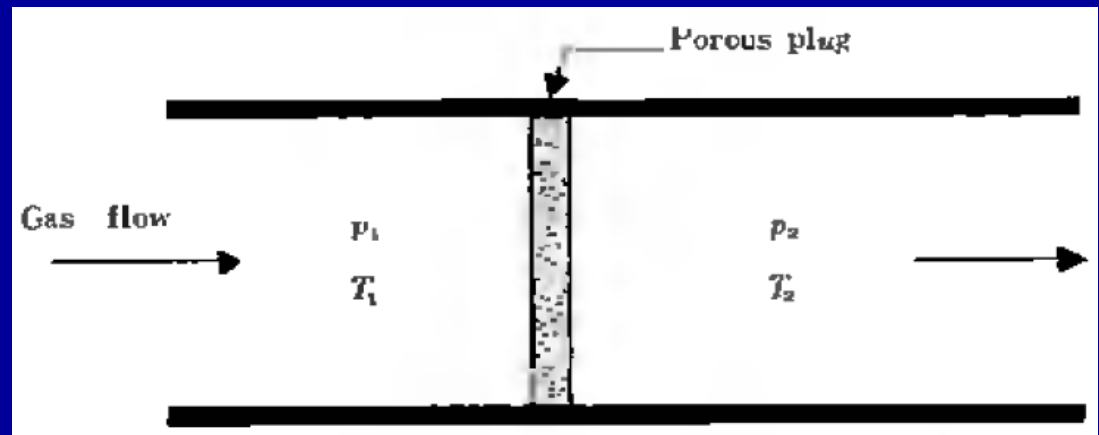
For an expansion where $v_2 > v_1$,

$$T_2 < T_1$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Steady-state experiment by J-T



A porous plug provide a constriction to the flow of gas;

A continuous stream of gas flow from left to right;
 p_1 in the left $>$ p_2 in the right;

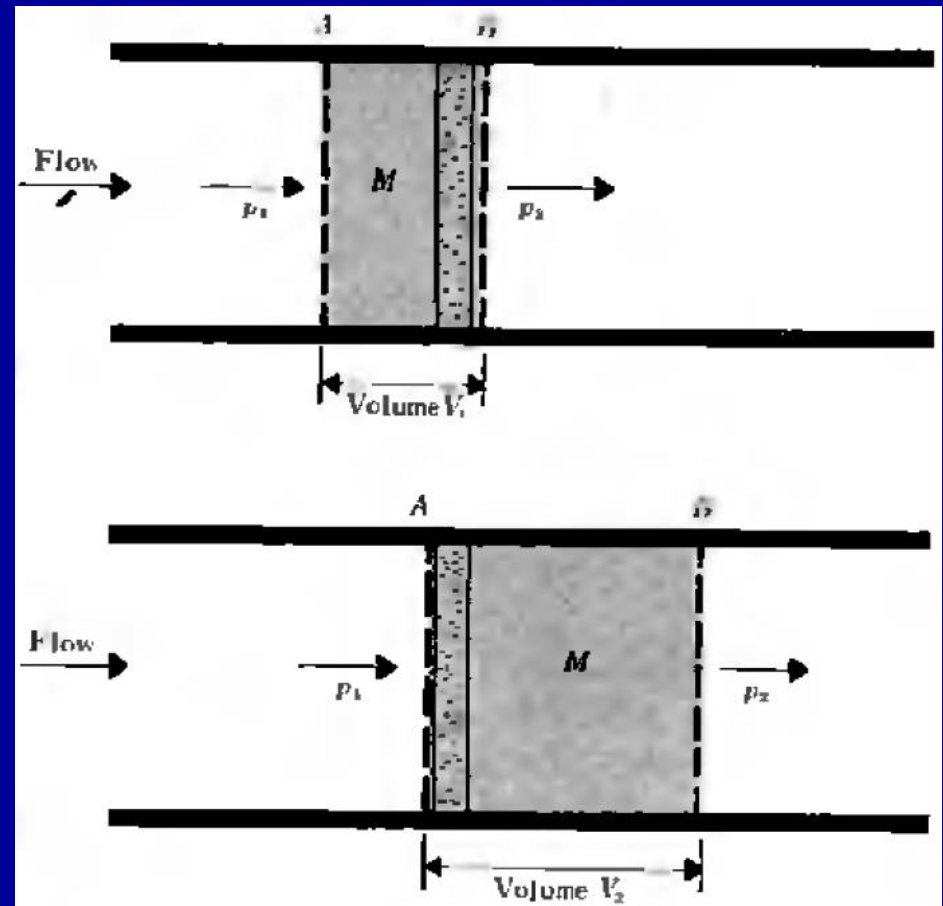
T_1 is the temperature in left, what is T_2 in right ?

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Initial: Left, p_1 , V_1

Final: right, p_2 , V_2



$$\Delta E = E_2 - E_1 = E(T_2, p_2) - E(T_1, p_1)$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

$$W = p_2 V_2 - p_1 V_1$$

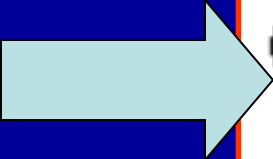
To external and by external

adiabatically insulated

$$Q = 0$$

Then,

$$\Delta E + W = Q = 0$$


$$(E_2 - E_1) + (p_2 V_2 - p_1 V_1) = 0$$
$$E_2 + p_2 V_2 = E_1 + p_1 V_1$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Already define

$$H \equiv E + pV$$

$$(E_2 - E_1) + (p_2V_2 - p_1V_1) = 0$$
$$E_2 + p_2V_2 = E_1 + p_1V_1$$

$$H(T_2, p_2) = H(T_1, p_1)$$

$$H = H(T)$$

For ideal gas

$$H = E + pV = E(T) + \nu RT$$

$$H(T_2) = H(T_1)$$

$$T_2 = T_1$$

in throttling process

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

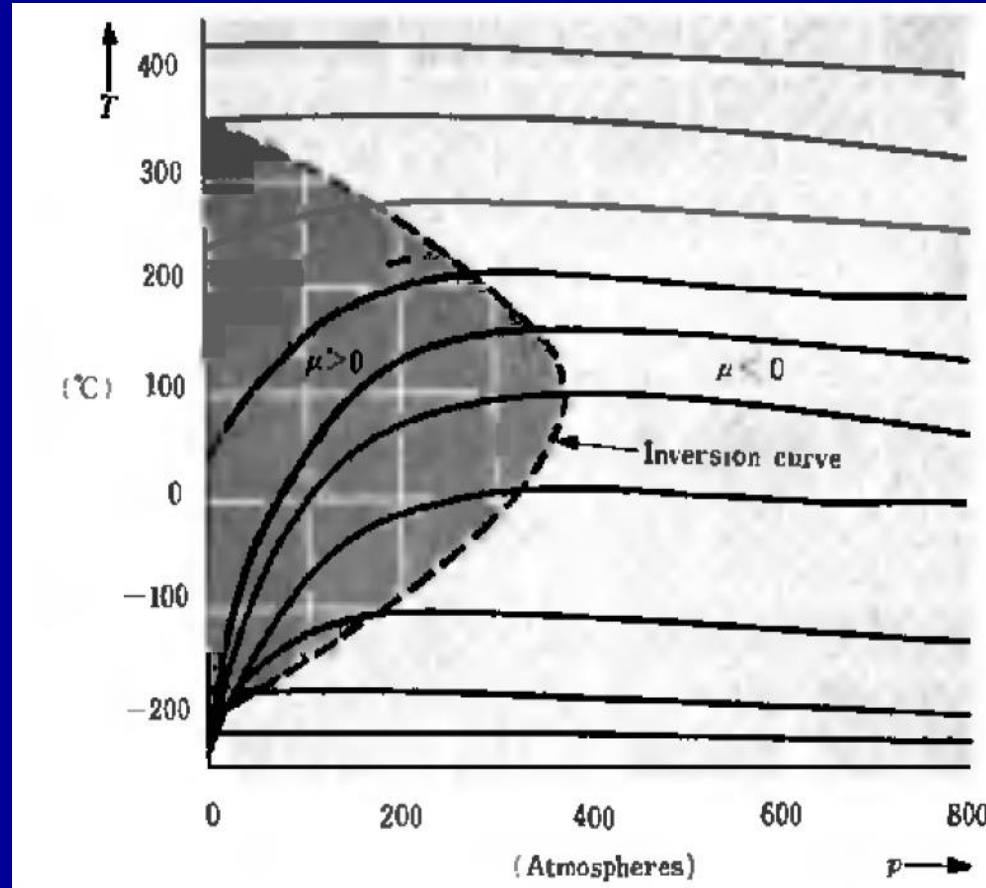
More generally, $H = H(T, p)$

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H$$

$\mu > 0$, T increases with p
 $\mu < 0$, T decreases with p

Inversion curve

$\mu == ??$



Free energy expansion and throttling process

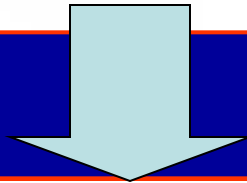
5.10 throttling process (Joule-Thomson ..)

$$dE = T dS - p dV$$

$$dH \equiv d(E + pV) = T dS + V dp$$

$$dH = 0.$$

$$C_p = T(\partial S / \partial T)_p.$$



$$0 = T \left[\left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \right] + V dp$$
$$C_p dT + \left[T \left(\frac{\partial S}{\partial p} \right)_T + V \right] dp = 0$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

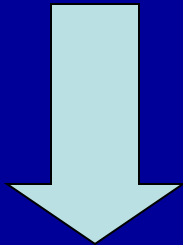
$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H$$

$$\mu \equiv \left(\frac{\partial T}{\partial p} \right)_H = - \frac{T(\partial S / \partial p)_T + V}{C_p}$$

Maxwell



$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p = -V\alpha$$



$$\mu = \frac{V}{C_p} (T\alpha - 1)$$

For ideal gas,

$$\alpha = T^{-1}$$



$$\mu = 0$$

Free energy expansion and throttling process

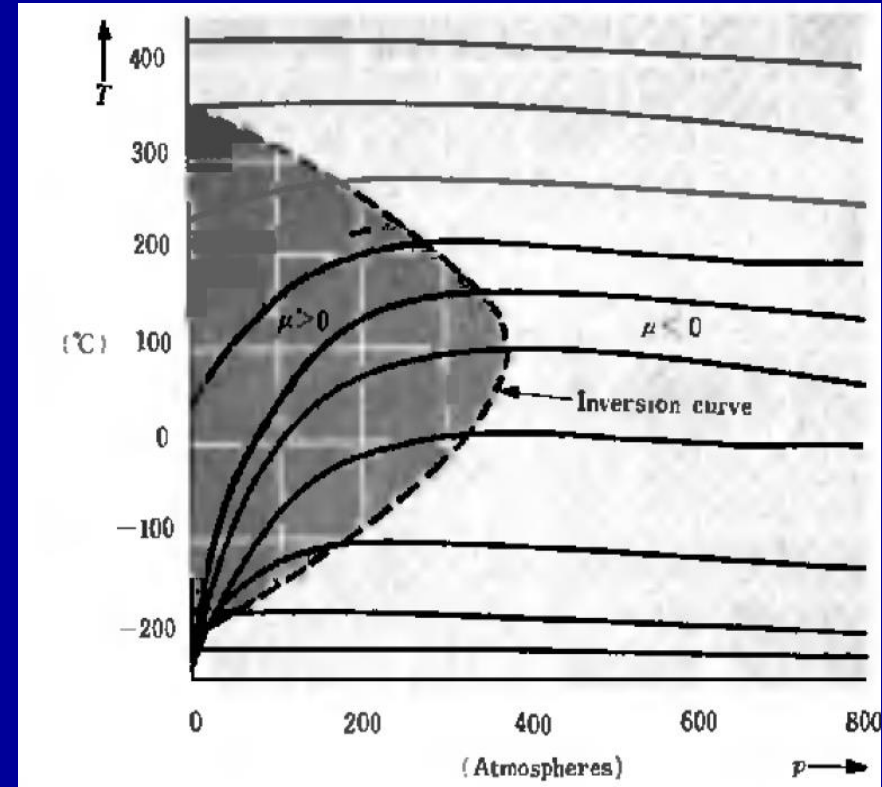
5.10 throttling process (Joule-Thomson ..)

Application:

J-T effect constitute a practical method for cooling gas .

1, It is necessary to work in the region of pressure and T where $\mu > 0$.

2, The initial $T < T_{\text{maximum}}$ on the inversion curve



Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Joule-Thomson effect and molecular force

For ideal gas,

T does not change for free expansion

..... for throttling process

These process becomes interesting for realistic gas
virial expansion

For any gas,

$$n \equiv N/V$$

$$p = kT[n + B_2(T)n^2 + B_3(T)n^3 \dots]$$

virial coefficient

$$p = \frac{N}{V} kT \left(1 + \frac{N}{V} B_2 \right)$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Joule-Thomson effect and molecular force

$$p = \frac{N}{V} kT \left(1 + \frac{N}{V} B_2 \right)$$

At low T, attractive force play dom. role, $B_2 < 0$;

At high T, (exclusion) collision play dom. role, $B_2 > 0$

 B_2 increases with T

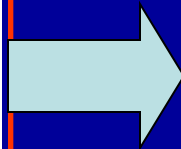
For nonideal gas, $\mu == ??$

Free energy expansion and throttling process

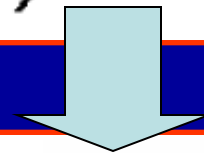
5.10 throttling process (Joule-Thomson ..)

Joule-Thomson effect and molecular force

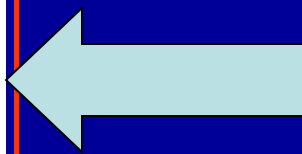
$$p = \frac{N}{V} kT \left(1 + \frac{N}{V} B_2 \right)$$



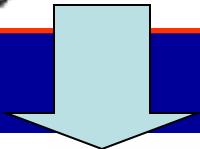
$$p = \frac{NkT}{V} \left(1 + \frac{p}{kT} B_2 \right) = \frac{N}{V} (kT + pB_2)$$
$$V = N \left(\frac{kT}{p} + B_2 \right)$$



$$\mu = \frac{V}{C_p} (T\alpha - 1)$$



$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$



$$\mu = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] = \frac{N}{C_p} \left(T \frac{\partial B_2}{\partial T} - B_2 \right)$$

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Joule-Thomson effect & molecular force: discussion

$$\mu = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] = \frac{N}{C_p} \left(T \frac{\partial B_2}{\partial T} - B_2 \right)$$

At low T, $B_2 < 0$, $\mu > 0$

At high T, $B_2 > 0$, μ can < 0

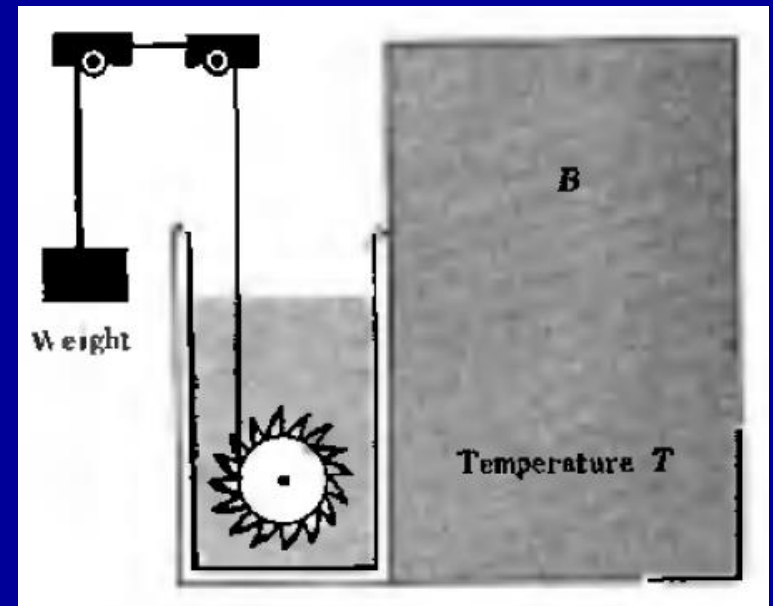
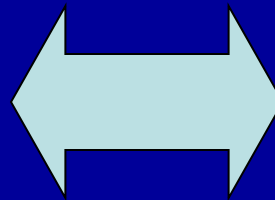
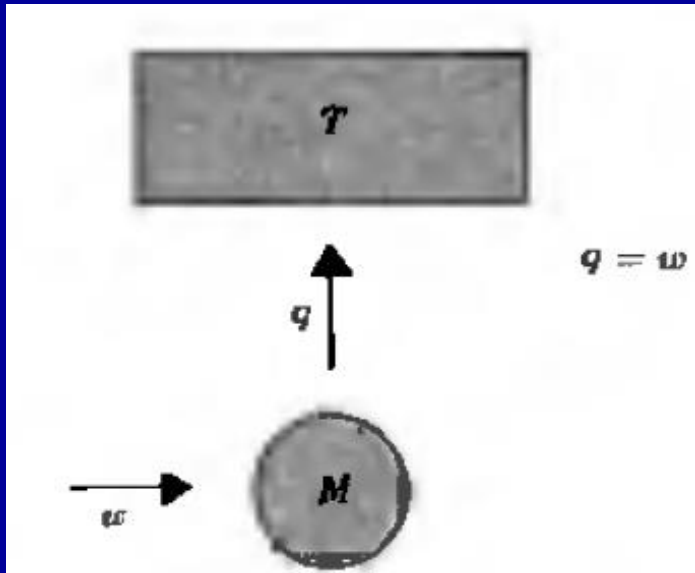
The inversion curve ($\mu=0$) indicates the competition between attraction and repulsion.

Heat engine and refrigerator

5.11 Heat engines

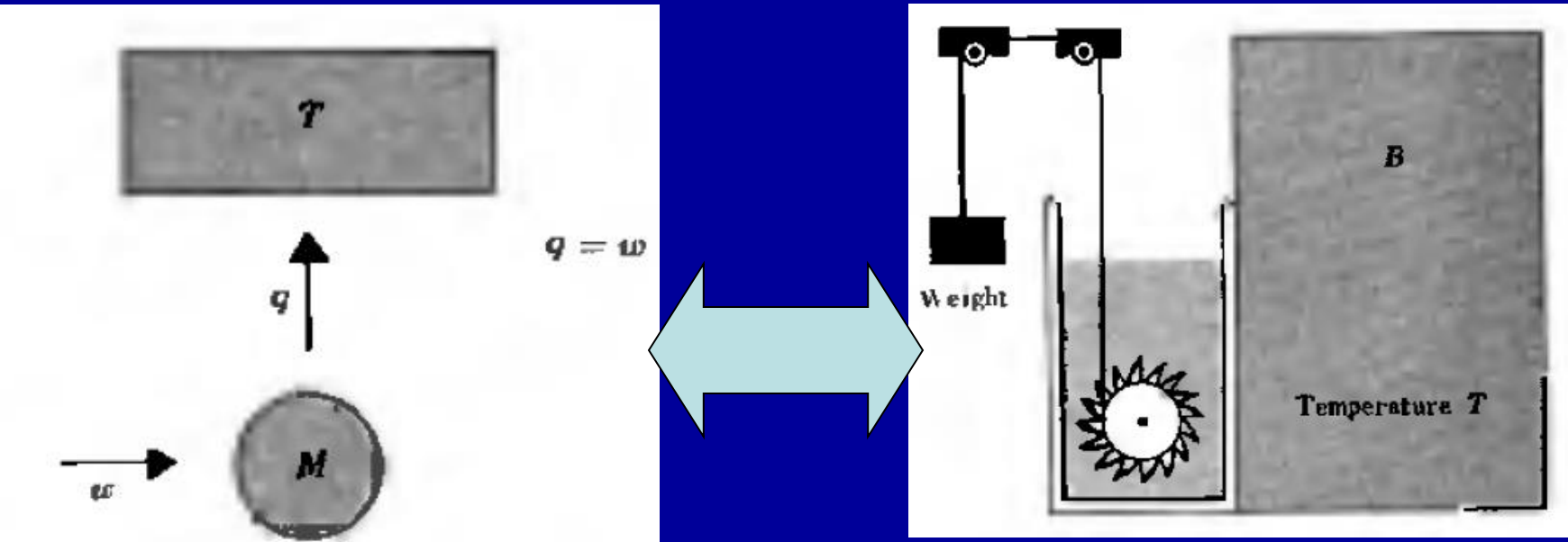
Historically, the subject of thermodynamics began with the study of engines:

- 1, great technological important
- 2, intrinsic physical interests



Heat engine and refrigerator

5.11 Heat engines



It is easy to do mechanical work w upon a device, and then extract from it heat q ($q=w$)

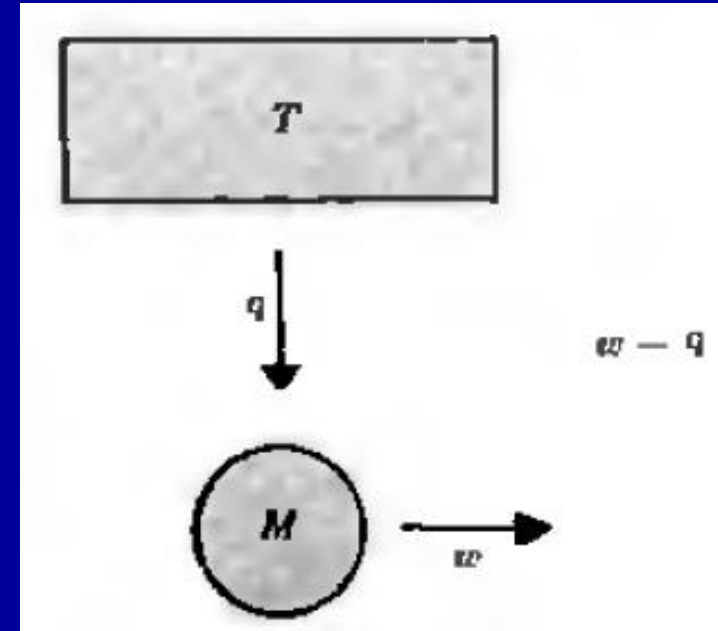
Heat engine and refrigerator

5.11 Heat engines

To what extent is it possible to proceed in the reversal way?

To build a device to extract internal energy from a heat reservoir in form of heat, and convert it to work?

The device is called **heat engine** !



Heat engine and refrigerator

5.11 Heat engines

Heat engine--- key points:

1, The work cannot be provided by the engine itself; or the heat-to-work process cannot be continued. Thus one wish the heat engine keeps the same macro-state at the end of process (cycle);

Heat engine and refrigerator

5.11 Heat engines

Heat engine--- Question?

To what extent is it possible to exact a net amount of energy from heat reservoir?

In reservoir, energy is randomly distributed over many degree of freedom.

To energy associated the single freedom connected with the external parameter.

Heat engine and refrigerator

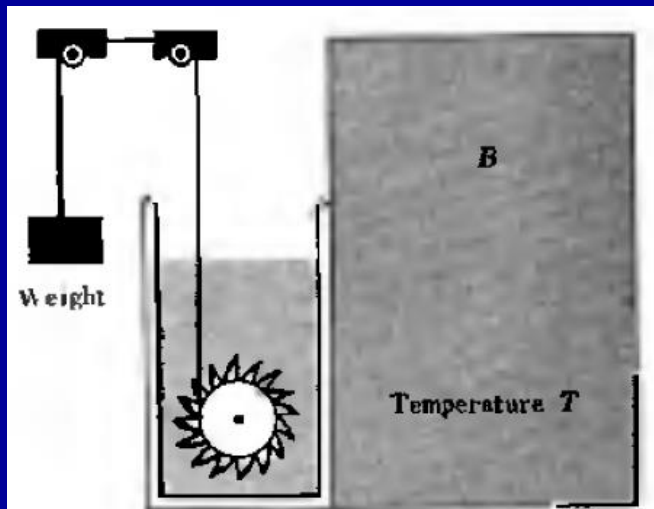
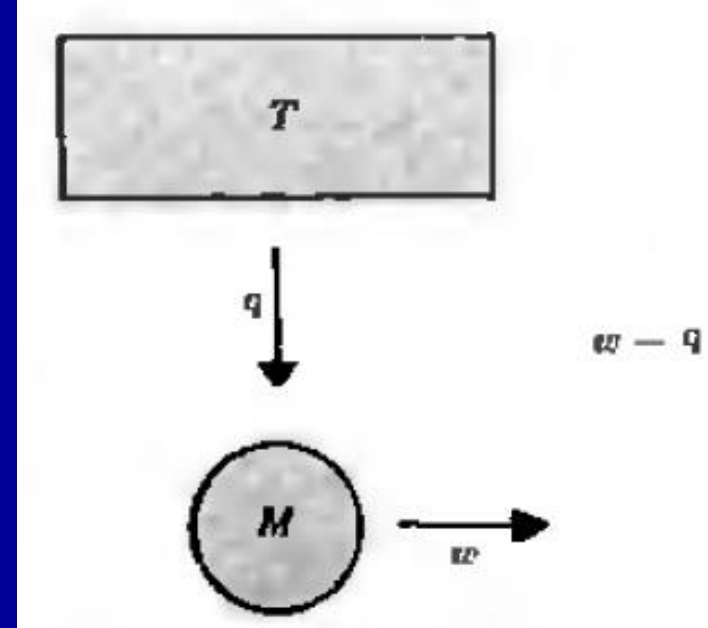
5.11 Heat engines

Heat engine--- Question?

First law \Rightarrow $w = q$
since E of M does not change

“perfect engine”

not realizable.



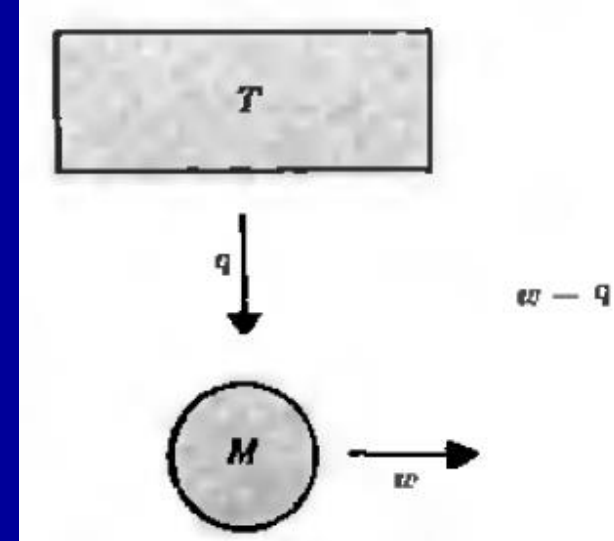
Work \rightarrow heat is an irreversible process
Since accessible states more random and entropy increases

Heat engine and refrigerator

5.11 Heat engines

Ideal heat engine violates 2nd law!

$$\Delta S \geq 0$$



Heat reservoir, absorbed heat == $(-q)$

The entropy change $-q/T_1$



$$\frac{-q}{T_1} \geq 0$$



$$\frac{q}{T_1} = \frac{w}{T_1} \leq 0$$

**Wish $w > 0$,
So it cannot be
satisfied!!!**

Heat engine and refrigerator

5.11 Heat engines

$$\frac{Q}{T_1} = \frac{w}{T_1} \leq 0$$

Wish $w > 0$,

So it cannot be satisfied!!!

It is impossible to construct a perfect heat engine.

————— Kelvin's formulation of the second law

Heat engine and refrigerator

5.11 Heat engines

Historically, the subject of thermodynamics began with the study of engines:

- 1, great technological importance
- 2, intrinsic physical interests

Class-work

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Homework

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