Chapter 5: Part C
Simple applications of macroscopic thermodynamics

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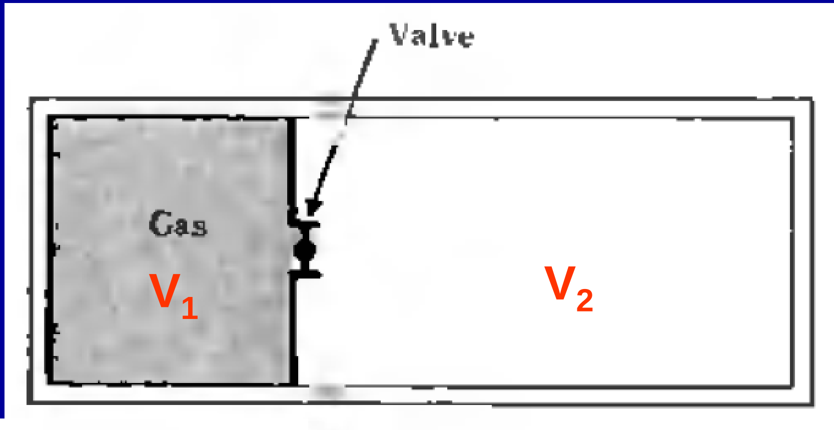
- **free expansion**
- **Throttling process**
- **heat engine**

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,

$$\boxed{Q = 0}$$

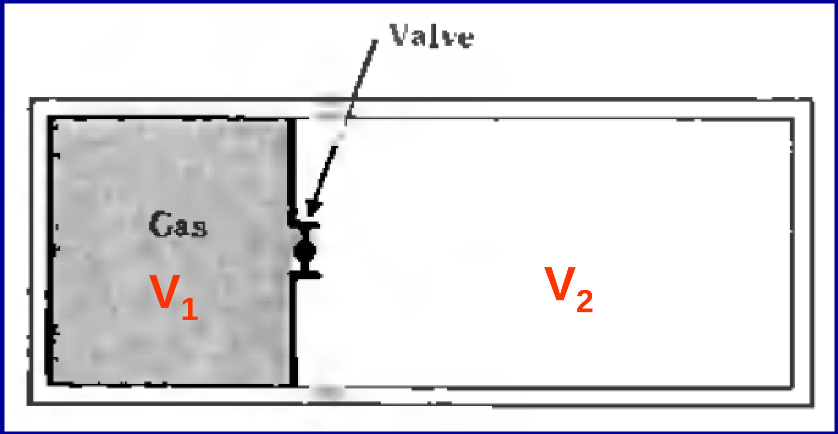
does no work in the process

$$\boxed{W = 0}$$

First law → $\boxed{\Delta E = 0}$

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 $E(T_2) = E(T_1)$ $\Rightarrow$ $\boxed{T_2 = T_1}$

Generally, $\boxed{E(T_2, V_2) = E(T_1, V_1)}$

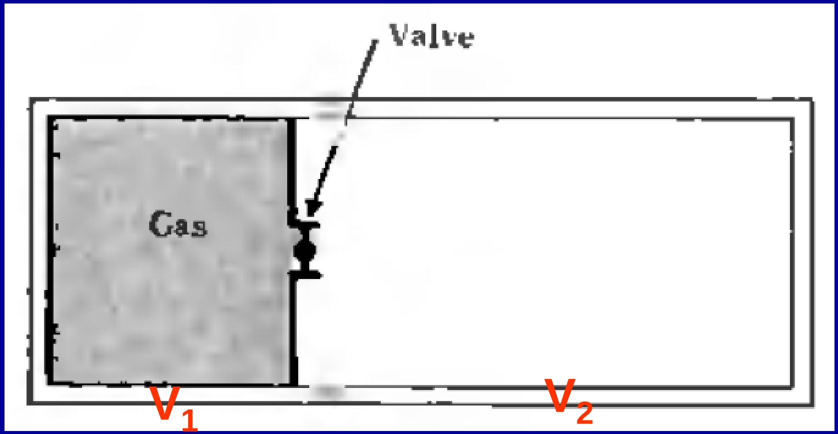
$$\Omega \propto V^N \chi(E)$$

$$\beta = \frac{\partial \ln \chi(E)}{\partial E}$$

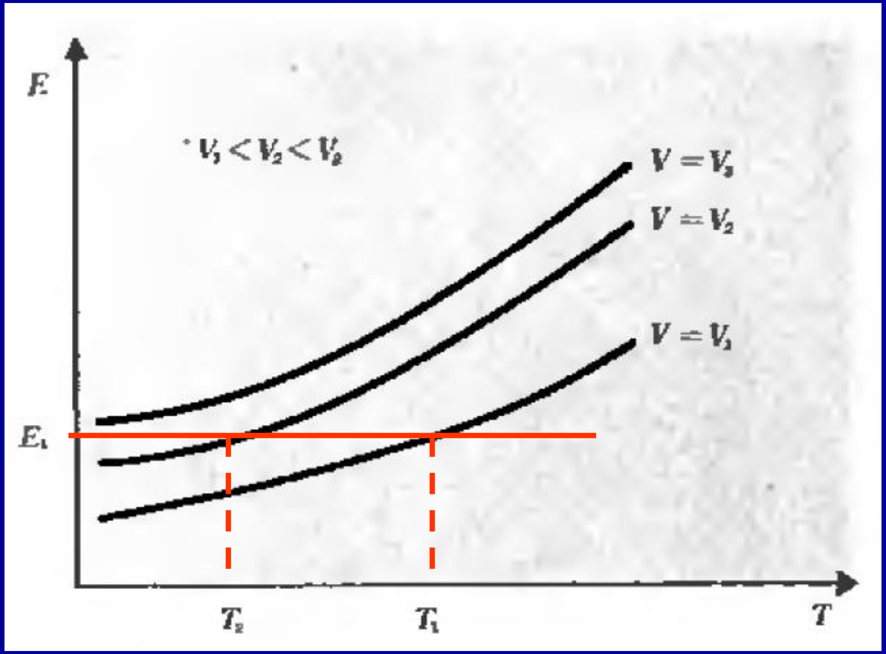
$$\beta = \beta(E)$$

Free energy expansion and throttling process

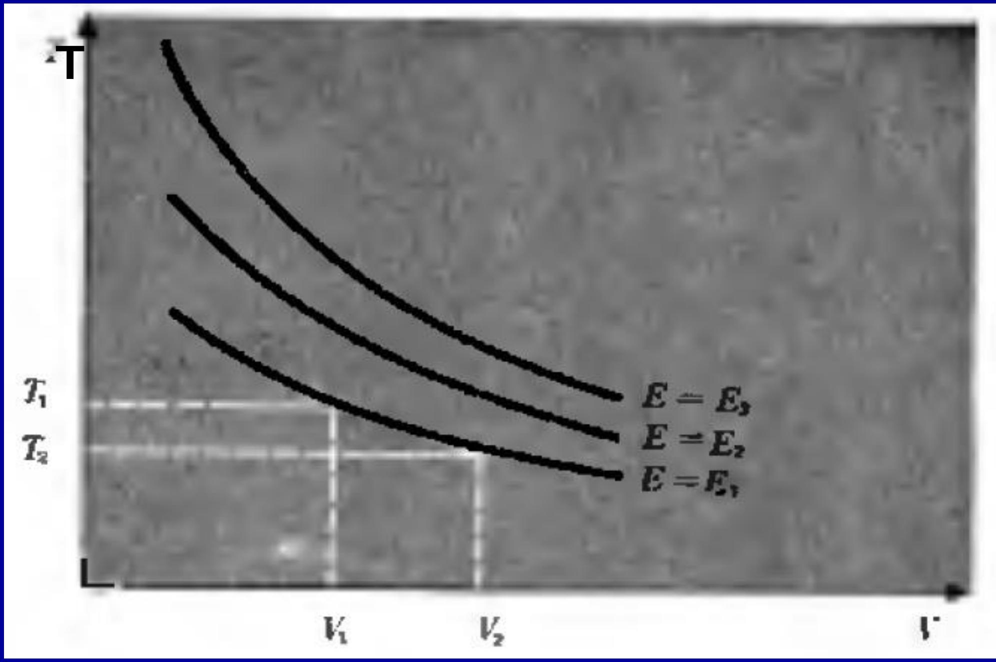
5.9 free expansion



E-T curve



V-T curve



Free energy expansion and throttling process

5.9 free expansion: example

Van de Waals gas

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

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

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

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

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

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 $[T_1, T_2]$

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

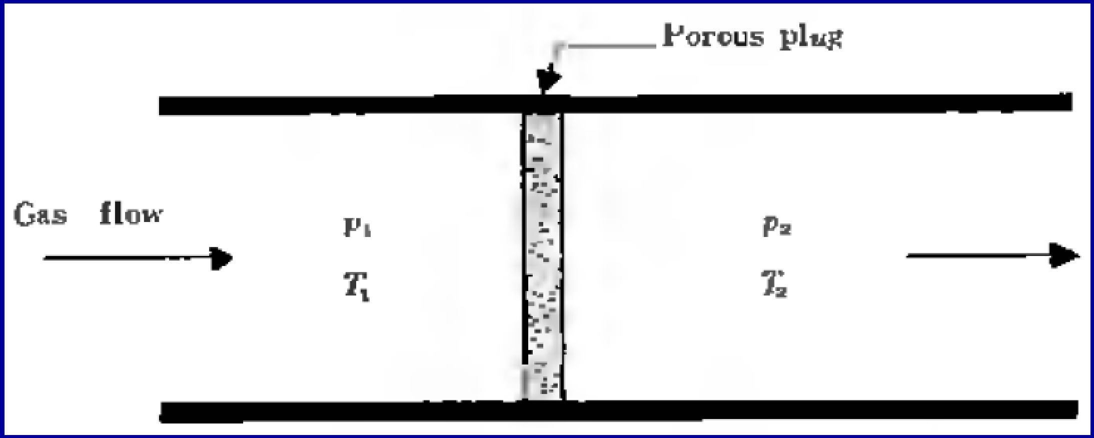
$$T_2 - T_1 = -\frac{a}{c_V}\left(\frac{1}{v_1} - \frac{1}{v_2}\right)$$

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;

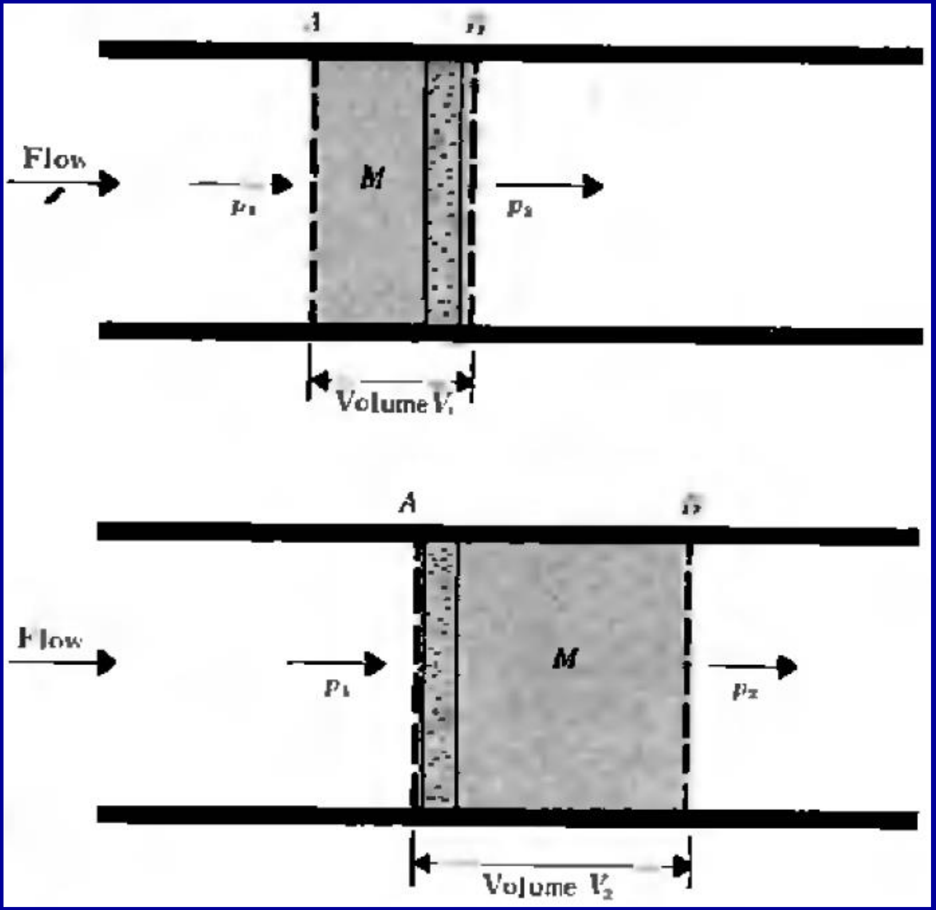
A continuous steam of gas flow from left to right;
p_1 in the left > p_2 in the right;

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 ..)

$$\boxed{W = p_2V_2 - p_1V_1}$$

To external and by external

adiabatically insulated

$$\boxed{Q = 0}$$

Then,

$$\boxed{\Delta E + W = Q = 0}$$

$$\boxed{\begin{gathered}(E_2 - E_1) + (p_2V_2 - p_1V_1) = 0 \\ E_2 + p_2V_2 = E_1 + p_1V_1\end{gathered}}$$

Free energy expansion and throttling process
5.10 throttling process (Joule-Thomson ..)

Already define $\boxed{H \equiv E + pV}$

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

$$\boxed{H(T_2,p_2) = H(T_1,p_1)}$$

$$H = H(T)$$

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

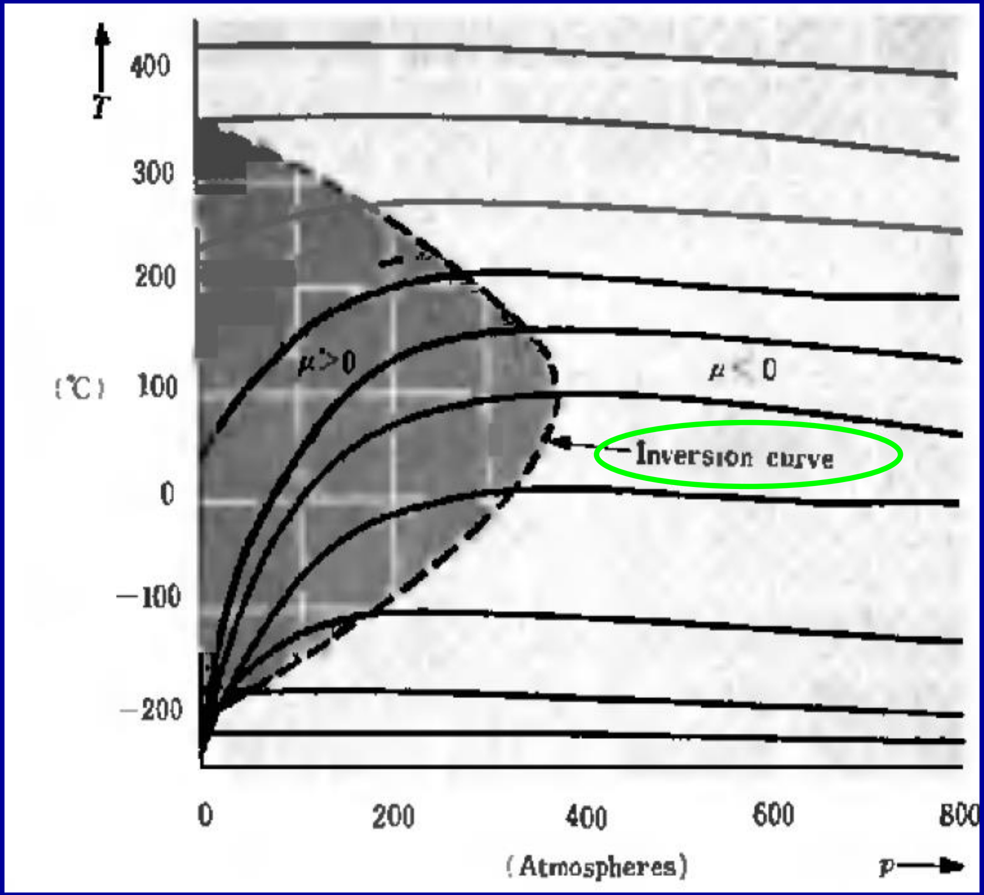
$$H(T_2) = H(T_1) \rightarrow \boxed{T_2 = T_1}$$

in throttling process

Free energy expansion and throttling process
5.10 throttling process (Joule-Thomson ..)

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

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



μ>0, T increases with p
μ<0, T decreases with p

Inversion curve

$$\mu == ??$$

Free energy expansion and throttling process
5.10 throttling process (Joule-Thomson ..)

1st law
2nd law

$$dE = T\,dS - p\,dV$$

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

$$dH = 0.$$

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

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

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

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

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

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

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

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

Maxwell

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

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

For ideal gas, $\alpha = T^{-1}$, $\Rightarrow$ $\mu = 0$

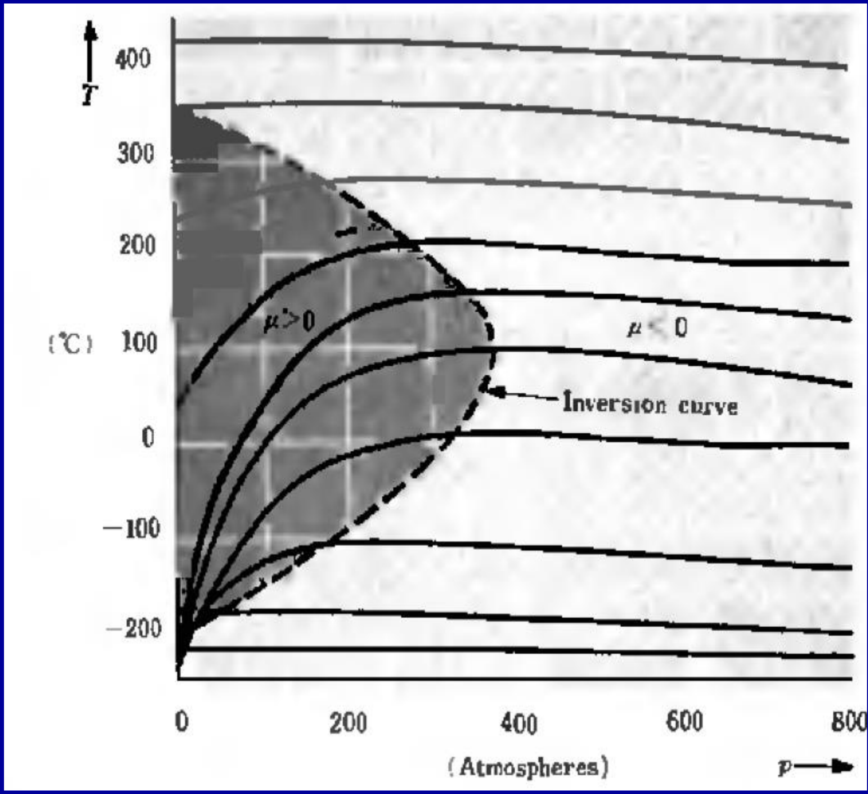
Free energy expansion and throttling process
5.10 throttling process (Joule-Thomson ..)

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 μ >0.

2, The initial T < T 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

For any gas,

$n \equiv N/V$

$$p = kT\underbrace{[n + B_2(T)n^2 + B_3(T)n^3 \cdots]}_{\text{virial expansion}}$$

virial coefficent

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

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, $B_2>0$

$\Rightarrow$ 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

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

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

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

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

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

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

Free energy expansion and throttling process

5.10 throttling process (Joule-Thomson ..)

Joule-Thomson effect & molecular force: discussion

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

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

At high T, $B_2>0$, μ can <0

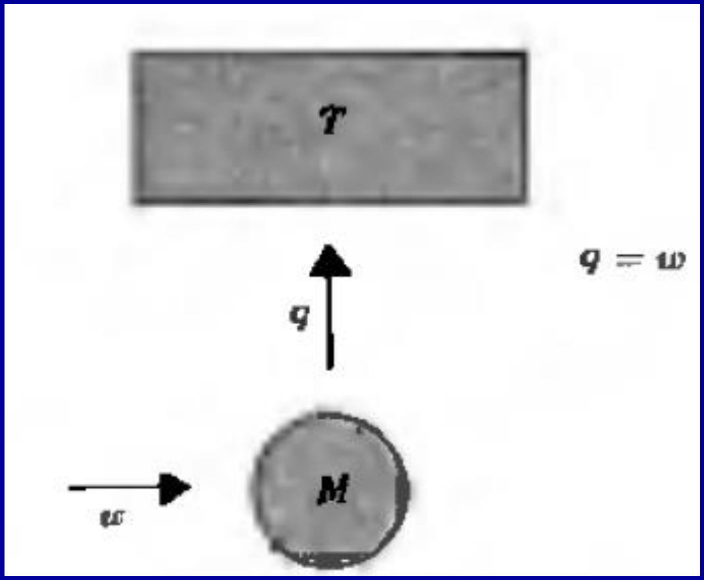
The inversion curve ($\mu=0$) indicates the competition between attraction and repulsion.

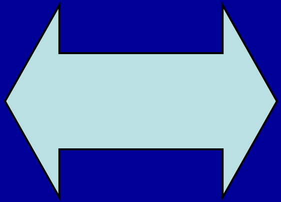
Heat engine and refrigerator
5.11 Heat engines

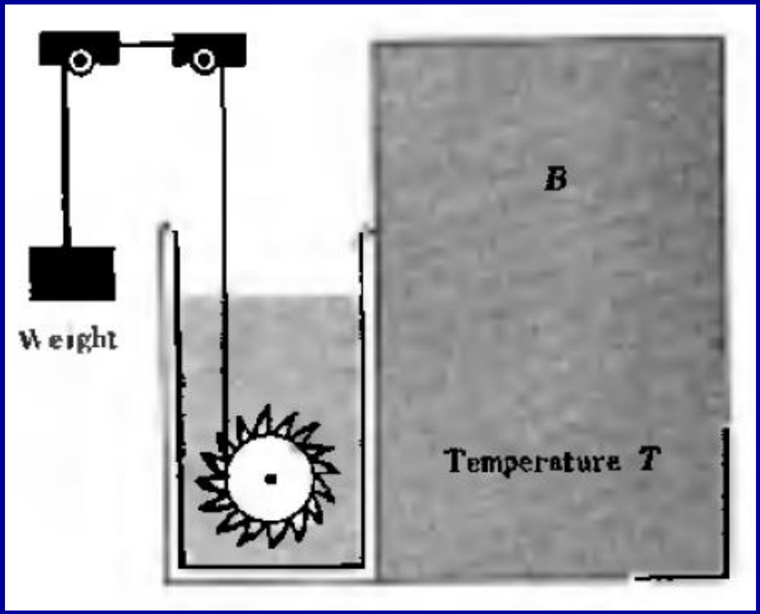
Historically, the subject of thermodynamics began with the study of engines:

1, great technological important

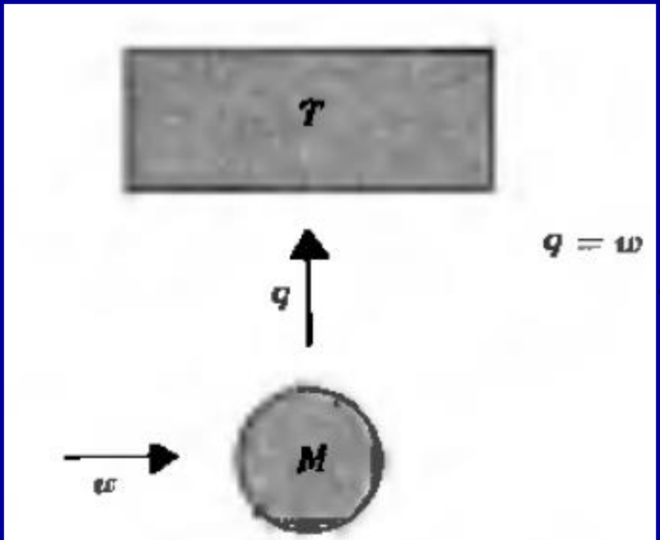
2, intrinsic physical interests

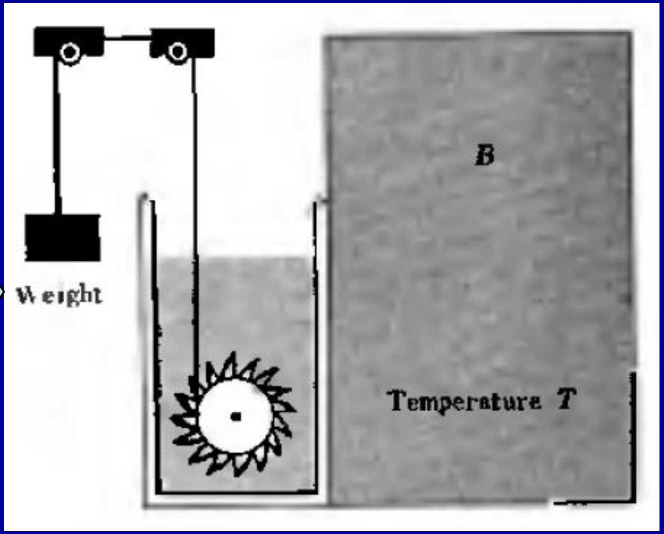






Heat engine and refrigerator
5.11 Heat engines

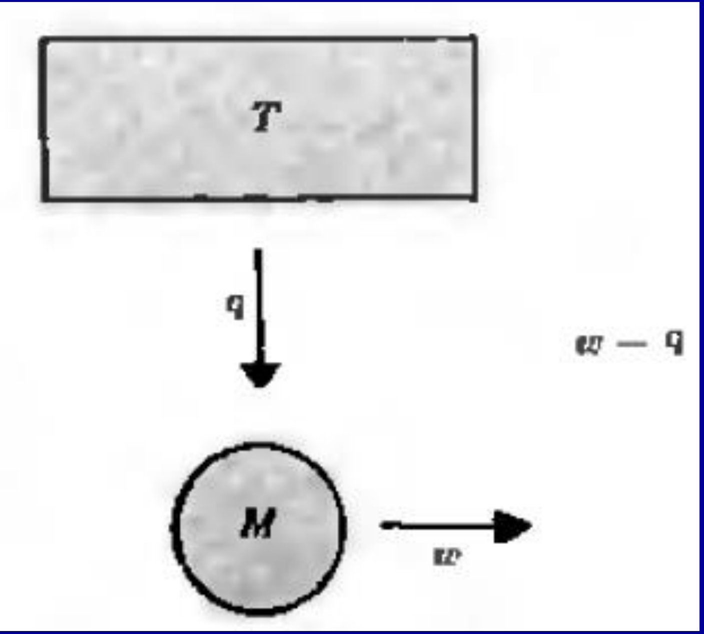




It is easy to do mechanical work *w* upon a device, and then extract from it heat *q* (*q*=*w*)

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 point:

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

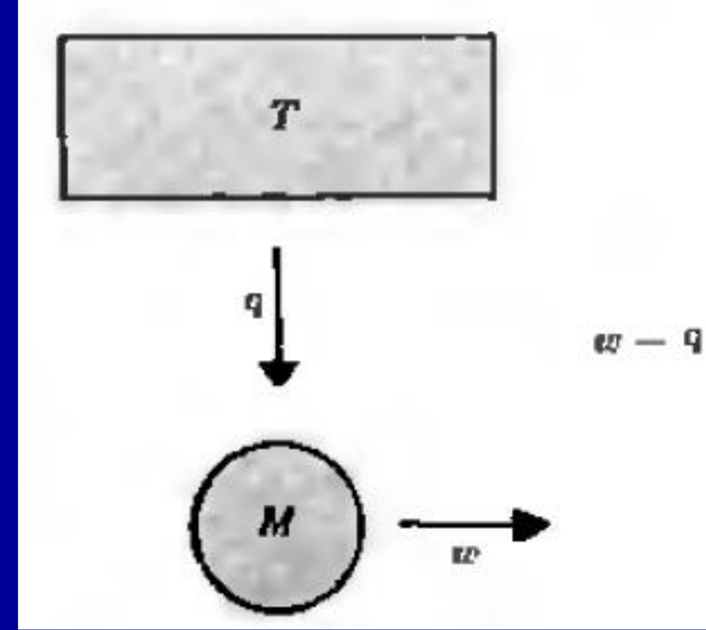
Heat engine--- Question?

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?

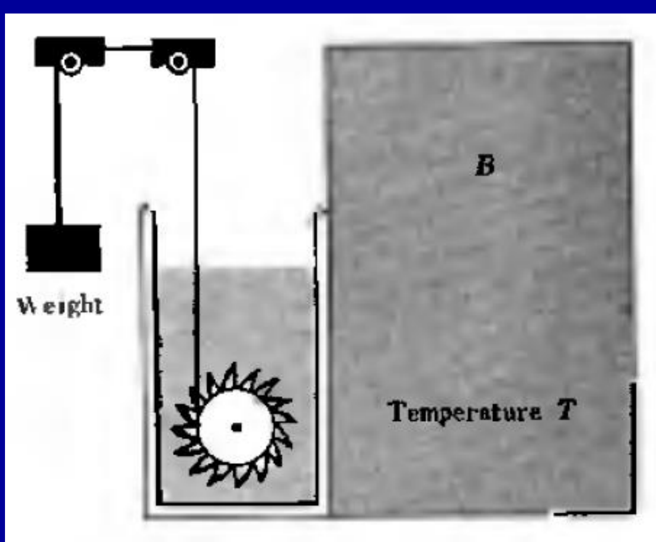
First law

$$w = q$$

since E of M does not change

"perfect engine"

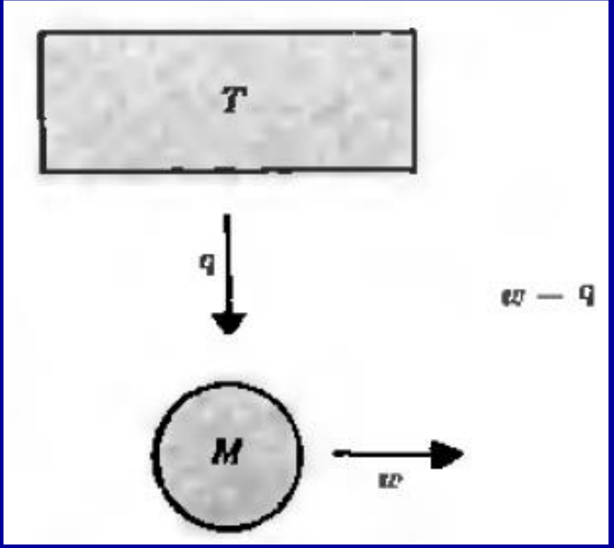
not realizable



Work→ 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

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

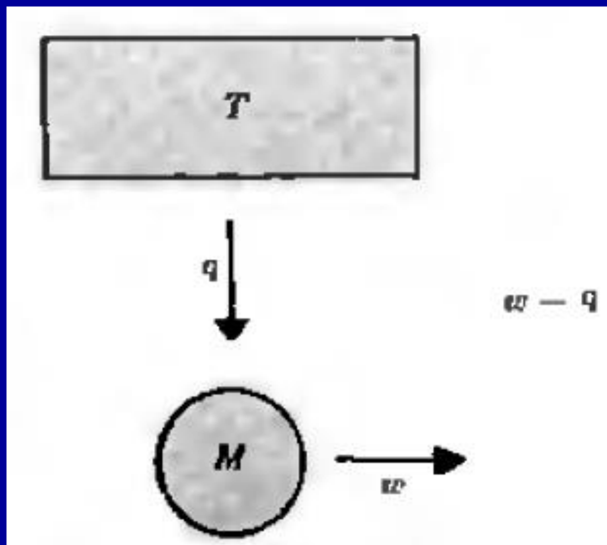
Wish w>0,

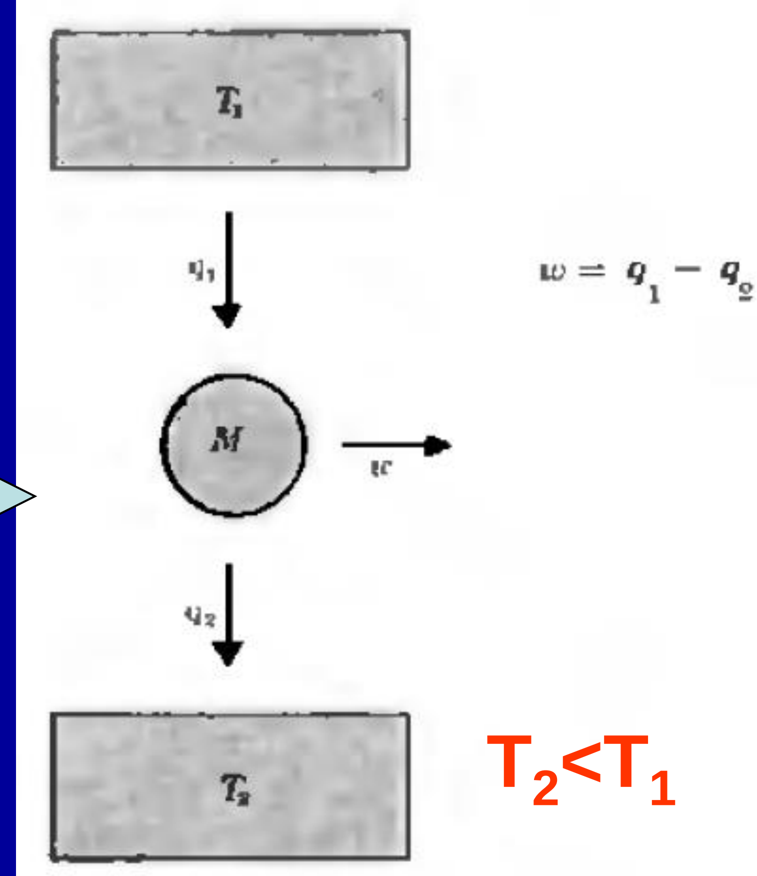
So it cannot be satisfied!!!

It is impossible to construct a perfect heat engine.

Kelvin's formulation of the second law

Heat engine and refrigerator
5.11 Heat engines: real





First law

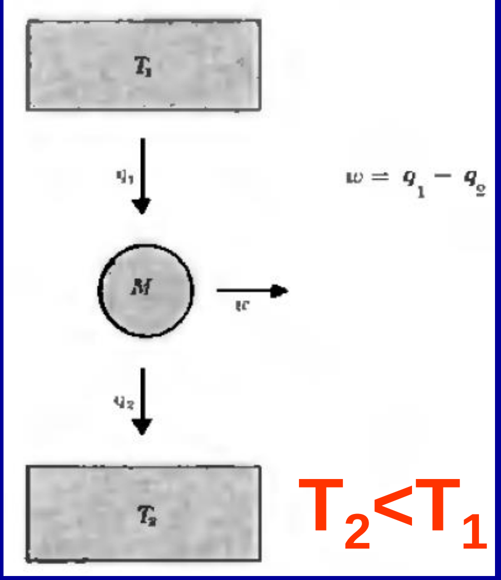
$$\boxed{q_1 = w + q_2}$$

2nd law

$$\boxed{\Delta S = \frac{(-q_1)}{T_1} + \frac{q_2}{T_2} \geq 0}$$

$$\boxed{\frac{-q_1}{T_1} + \frac{q_1 - w}{T_2} \geq 0}$$

Heat engine and refrigerator
5.11 Heat engines: real



$T_2 < T_1$

First law **2nd law**

$$\frac{-q_1}{T_1} + \frac{q_1 - w}{T_2} \geq 0$$

$$\frac{w}{T_2} \leq q_1\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\eta = \frac{T_1 - T_2}{T_1}$$

Define

$$\eta \equiv \frac{w}{q_1} \leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Efficiency of heat engine

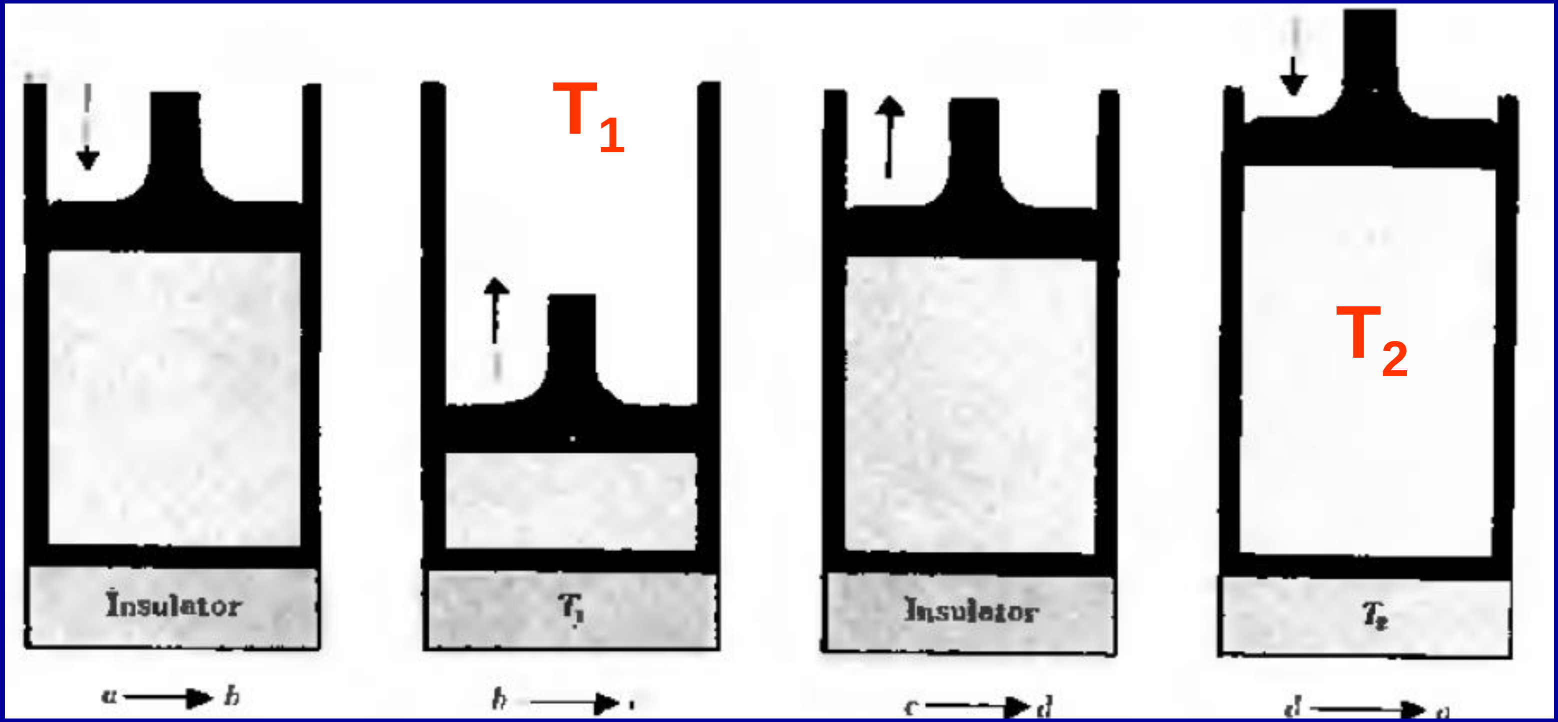
if quasi-static,

$$\eta = \frac{T_1 - T_2}{T_1}$$

Heat engine and refrigerator

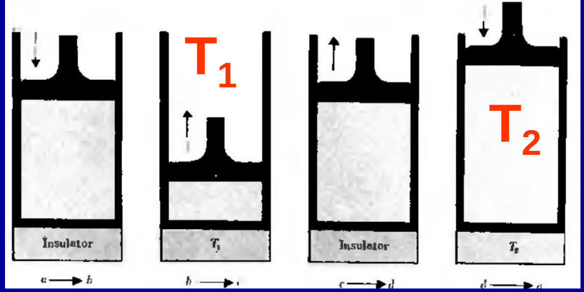
5.11 Carnot engines

How does such a engine operate quasi-statically between two heat reservoirs ?



thermally insulted | thermal Contact T_1 | thermally insulted | thermal Contact T_2

Heat engine and refrigerator
5.11 Carnot engines: process



1. $a \to b$: The engine is *thermally insulated*. Its external parameter is changed slowly until the engine temperature reaches T_1. Thus $x_a \to x_b$ such that $T_2 \to T_1$.

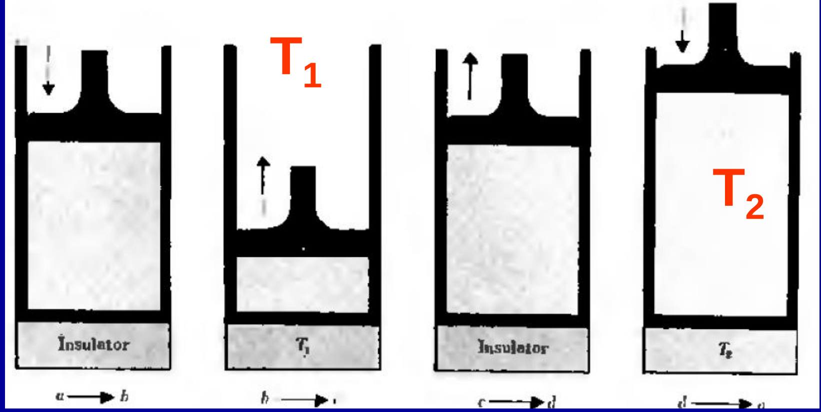
2. $b \to c$: The engine is now placed in *thermal contact* with the heat reservoir at temperature T_1. Its external parameter is changed further, the engine remaining at temperature T_1 and absorbing some heat q_1 from the reservoir. Thus $x_b \to x_c$ such that heat q_1 is absorbed by the engine.

3. $c \to d$: The engine is again *thermally insulated*. Its external parameter is changed in such a direction that its temperature goes back to T_2. Thus $x_c \to x_d$ such that $T_1 \to T_2$.

4. $d \to a$: The engine is now placed in *thermal contact* with the heat reservoir at temperature T_2. Its external parameter is then changed until it returns to its initial value x_a, the engine remaining at temperature T_2 and rejecting some heat q_2 to this reservoir. Thus $x_d \to x_a$ and heat q_2 is given off by the engine.

The engine is now back in its initial state and the cycle is completed.

Heat engine and refrigerator
5.11 Carnot engines: process



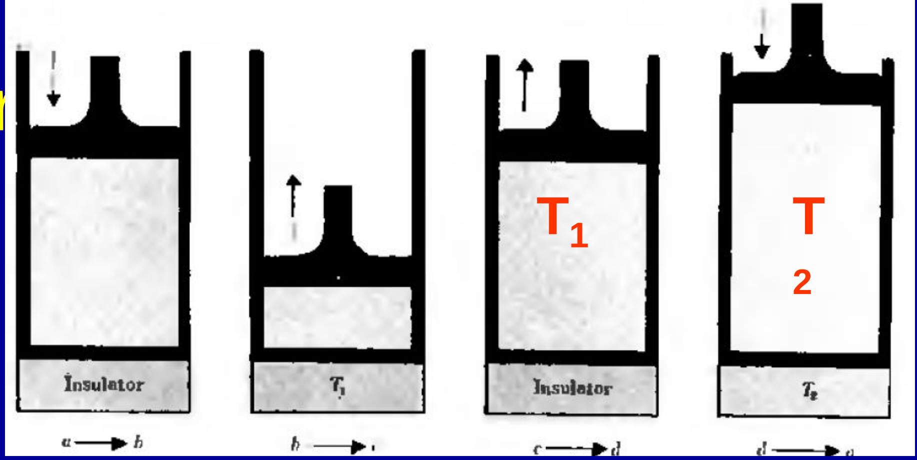
$a \to b$; thermally insulted; compression; $T_2 \to T_1; q = 0$

$b \to c$; thermal contact with T_1; expansion; q_1

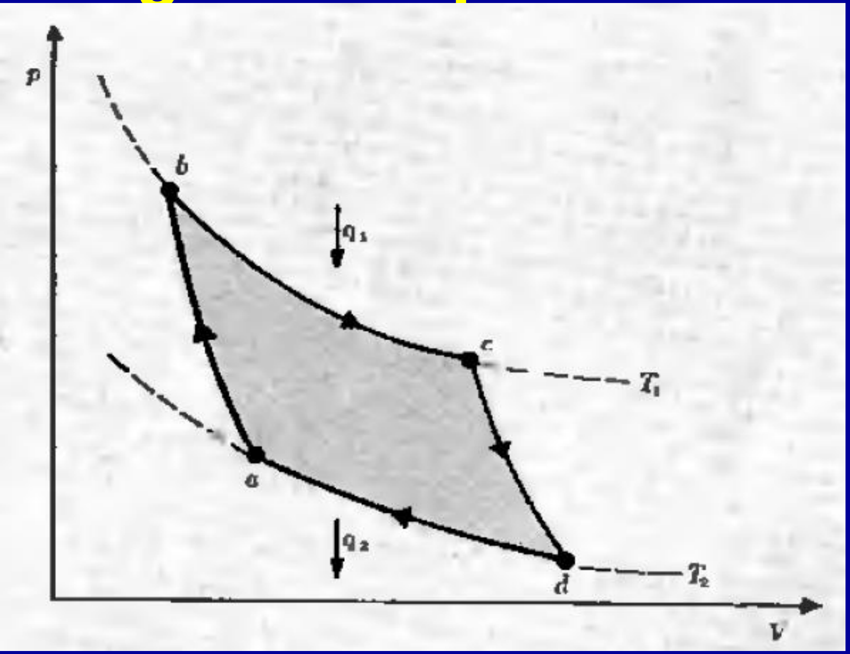
$c \to d$; thermally insulted; expansion; $T_1 \to T_2; q = 0$

$d \to a$; thermal contact with T_2; compression; $-q_2$

Heat engine and refrigerator



5.11 Carnot engines: Diagram on pV



$$\boxed{w = \int_a^b p\,dV + \int_b^c p\,dV + \int_c^d p\,dV + \int_d^a p\,dV}$$

$$\eta \equiv \frac{w}{q_1} \leq 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Heat engine and refrigerator

5.11 Refrigerator

Remove heat from reservoir at low T to that at high T

First law $\boxed{w + q_2 = q_1}$

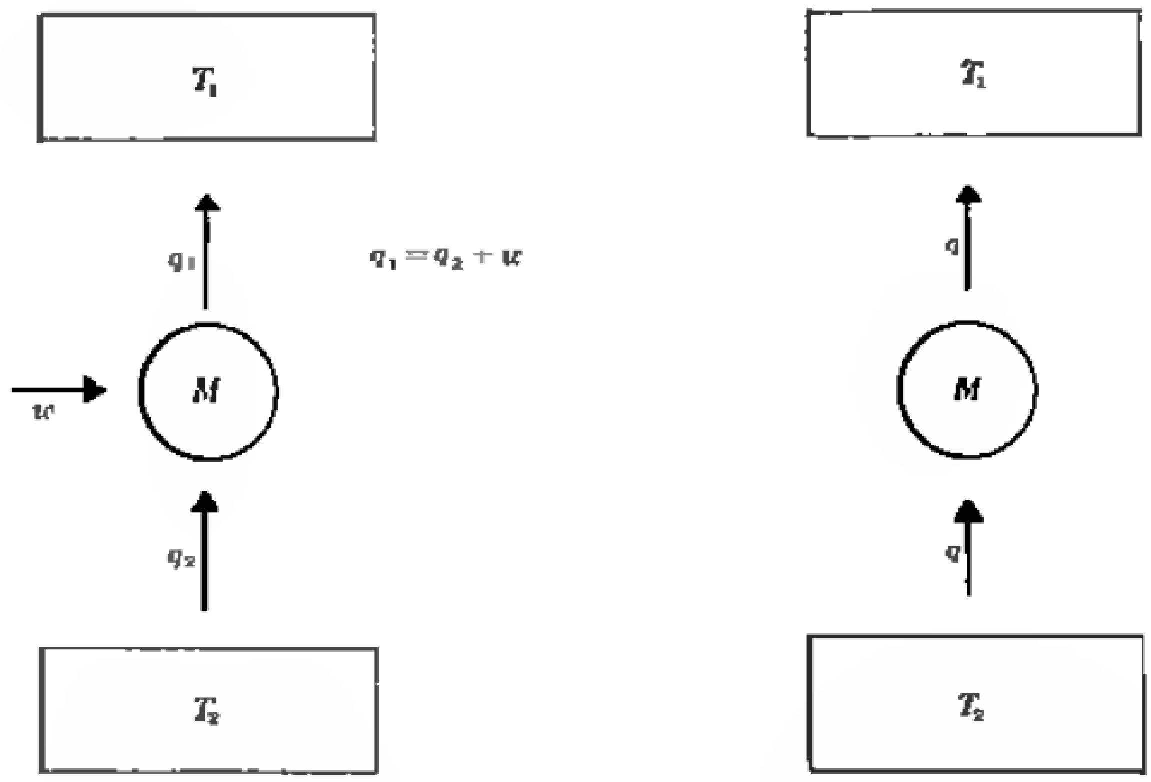


Fig. 5·12·1 A real refrigerator. Fig. 5·12·2 A perfect refrigerator.

Heat engine and refrigerator

5.11 Refrigerator

Remove heat from reservoir at low T to that at high T

Perfect refrigerator

$$\Delta S = \frac{q}{T_1} + \frac{(-q)}{T_2} \geq 0$$

$$q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0$$

impossible for $q > 0$ and $T_1 > T_2$.

It is impossible to construct a perfect refrigerator.

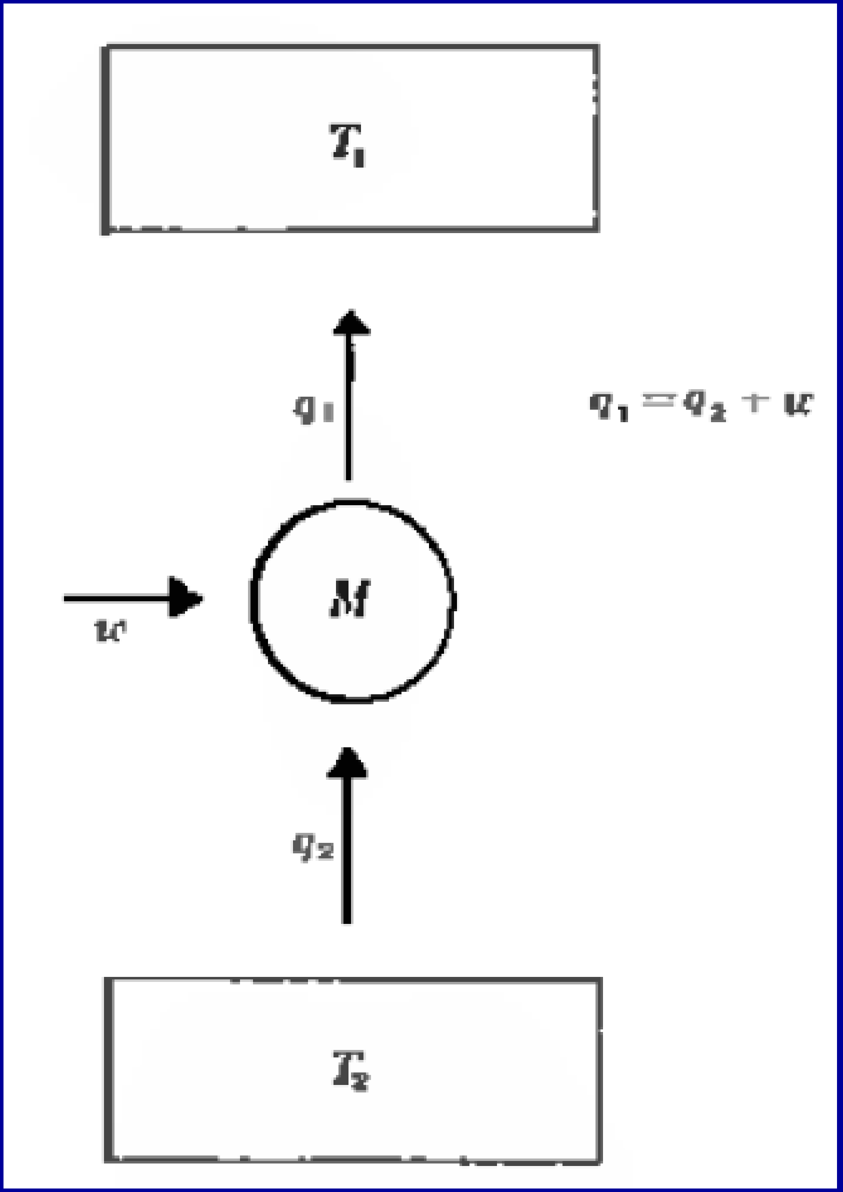
the Clausius formulation of the second law

Heat engine and refrigerator
5.11 Refrigerator: real

First law $q_2 = q_1 - w$

2nd law
$$\Delta S = \frac{q_1}{T_1} + \frac{(-q_2)}{T_2} \geq 0$$
$$\frac{q_2}{q_1} \leq \frac{T_2}{T_1}$$

$$\boxed{\begin{aligned} \varepsilon &= \frac{q_2}{w} = \frac{q_2}{q_1 - q_2} = \frac{1}{q_1/q_2 - 1} \\ &\leq \frac{1}{T_1/T_2 - 1} = \frac{T_2}{T_1 - T_2} \end{aligned}}$$



Class-work

P 198   5.26

Homework

P 192 5.18,5.20,5.23,5.24