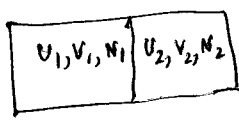


# Energy minimum principle [Callan Section 5.1] <sup>32</sup>

We have already used the postulates to get the entropy maximum principle. In detail

$S(U, V, N)$  is a maximum on removal of a constraint, for a fixed value of internal energy

## Example



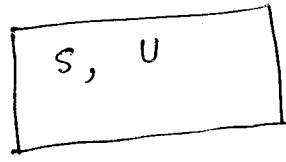
$U = U_1 + U_2$  fixed.

On allowing the ~~constraint~~ of partition, there are several possible values of  $V_1$  (we are keeping  $N_1$  fixed) and the one in which equilibrium is reached is the one for which  $S$  is a maximum.

## Energy minimum principle

The equilibrium value of any unconstrained parameter (like volume, number of components) is such that the energy is a minimum for a given value of entropy.

## Proof



Let  $U$  not be a minimum

Then we can change the system to  $(S, U - \Delta U)$  with  $\Delta U$  in the form of work (by a suitable process)  $\Delta U$  can be given back to the system in the form of heat (by another suitable process) and this will change the entropy to  $S + \Delta S$  with internal energy  $U$ .  $\Rightarrow$  Violation of the maximum

Consider a closed system with two subsystems separated by a rigid conducting wall (heat is allowed to flow) but  $N$  and  $V$  are fixed

$$U = U^{(1)}(S^{(1)}, V^{(1)}, N^{(1)}, \dots) + U^{(2)}(S^{(2)}, V^{(2)}, N^{(2)}, \dots)$$

$$dU = T^{(1)} dS^{(1)} + T^{(2)} dS^{(2)} = 0$$
$$= (T^{(1)} - T^{(2)}) dS^{(1)} = 0 \quad \text{or} \quad T^{(1)} = T^{(2)}$$

### Thermodynamic Potentials

In general  $\frac{\Delta Q}{T} \leq \Delta S$  or  $\Delta Q \leq T \Delta S$

Thus  $T \Delta S \geq \Delta U + \Delta W_{\text{by}}$

$P \Delta V$  (W.D by the systk)

Equality for a reversible process.

For a fixed states  $A$  and  $B$   $U_A$  &  $U_B$  are fixed. The maximum work that can be extracted is  $T \Delta S$ ; and that for the reversible process,

Consider the quantity called Free energy [Helmholtz]  
 $F = U - TS$

$$\Delta F = \Delta U - T \Delta S - S \Delta T \leq \Delta U - \Delta Q - S \Delta T$$

$\Delta Q = \Delta U + \Delta W_{\text{by}}$

$$\Delta F \leq -\Delta W_{\text{by}} - S \Delta T$$

Consider an isothermal transformation from  $A$  to  $B$  ( $\Delta T = 0$ )

if  $\Delta F \geq 0$   $F(B) - F(A) > 0$

$$\Delta W_{\text{on}} \geq F(B) - F(A)$$

One has to do work on the system to increase its free energy, the minimum is for the reversible case. In general more work has to be done

(reversible)  $= \Delta W(\text{dissipation})$

$$\text{If } F(B) < F(A)$$

$$\Delta W_{by} \leq F(A) - F(B)$$

This is the maximum energy we can get from the transition occurs from A to B [maximum when it is carried out reversibly].

### Enthalpy

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

Consider a reservoir having a constant pressure. The system is in contact with the reservoir with a movable piston. The system + reservoir is a closed system. [Adiabatic]  $\Delta U_s + \Delta U_r = 0$

$$\Delta U^r = \left( \text{Because the System does work on the system} \right)$$

$$= -P^r \Delta V^r = P^r \Delta V^s.$$

$$\Delta U^s + \Delta U^r = 0$$

$$\Delta (U + P^r V) = 0$$

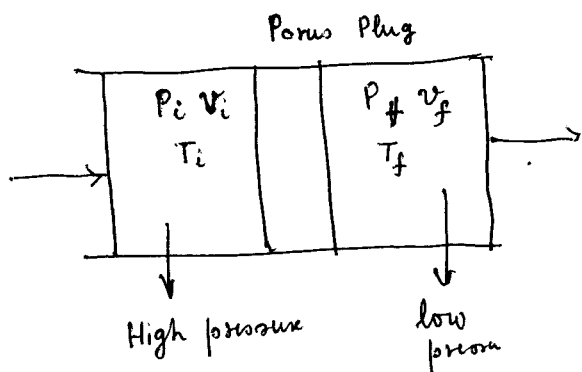
If the system is in equilibrium with the reservoir initially at finally

$$\Delta (U + P^r V) = 0$$

This is used in Joule-Thomson effect.

# Joule-Thomson process

36  
35



A system is maintained at constant pressure and its volume changed from  $V_i$  to  $V_f$  by allowing it to be in touch with a reservoir and a movable piston the heat flux

$$\Delta Q = \Delta U + \Delta(PV) = \Delta H$$

$$\int \Delta Q = H_f - H_i$$

Suppose we know the ~~fundamental~~ equation  $H(S, P, N)$

$$\left. \frac{\partial [H]}{\partial P} \right|_{S, N} = \left. \frac{dU + PdV + VdP}{dP} \right|_{S, N} = \left. \frac{TdS + VdP}{dP} \right|_{S, N} = V(S, P, N)$$

Eliminate  $S$  in favour of  $V$ .

$$\int \Delta Q = H(V_f, P, N) - H(V_i, P, N)$$

Consider one mole of gas (single component) pushing the quant it across the porous plug

w.D  $P_i V_i$  and w.D on the other side is  $P_f V_f$

$$u_f = u_i + P_i V_i - P_f V_f \Rightarrow h_f = h_i$$

The change in temperature

$$dT = \left. \frac{\partial T}{\partial P} \right|_{h, N} dP = - \frac{\left. \frac{\partial H}{\partial P} \right|_T}{\left. \frac{\partial H}{\partial T} \right|_P} dP$$

$$dH = Tds + vdp = 0$$

$$T \left( \frac{\partial s}{\partial p} \right)_T dp + T \left( \frac{\partial s}{\partial T} \right)_{H,P} dT + v dp = 0$$

$$dT = - \frac{T \left( \frac{\partial s}{\partial p} \right)_T + v}{T \left( \frac{\partial s}{\partial T} \right)_P} dp$$

$$\frac{S}{V} \frac{P}{T}$$

(36)

$$\left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_P$$

$$\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P$$

$$dT = \frac{v}{C_p} [T\alpha - 1] dp$$

For ideal gas  $\alpha = \frac{1}{PV} \frac{\partial RT}{\partial T} = \frac{R}{PV} = \frac{1}{T}$

$$dT = 0$$

On the other hand

The quantity

$$\left( \frac{dT}{dp} \right)_H = - \frac{T \left( \frac{\partial s}{\partial p} \right)_T + v}{T \left( \frac{\partial s}{\partial T} \right)_P} = \mu = \frac{T \left( \frac{\partial v}{\partial T} \right)_P - v}{C_p}$$

For any gas we can write

$$pV = \cancel{RT(N + B_2(T))} N RT \left( 1 + B_2 \left( \frac{N}{V} \right) + B_3 \left( \frac{N}{V} \right)^2 + \dots \right)$$

$B_2, B_3$  are called virial co-efficients.

First correction  $B_3 = B_4 = 0 \dots$

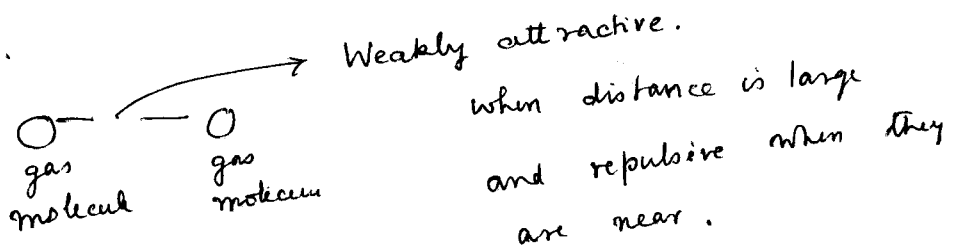
$$p = \frac{NkT}{V} \left( 1 + B_2 \frac{p}{kT} \right) \quad \text{Use } \frac{N}{V} = \frac{p}{kT}$$

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

$$T \left( \frac{\partial V}{\partial T} \right)_P - V = \frac{NkT}{p} + N \frac{\partial B_2}{\partial T} - \frac{NkT}{p} - NB_2 \quad (38)$$

$$\mu = \frac{N}{C_p} \left( T \frac{\partial B_2}{\partial T} - NB_2 \right) \quad (37)$$

Physical considerations to understand the nature of  $B_2$ .



Attraction tends to reduce the pressure.

So  $B_2 < 0$

At high temperatures, molecules come closer and

then  $B_2 > 0$

Thus one expects  $\frac{dB_2}{dT} > 0$

At high temperatures  $\mu$  can be -ve.

We will discuss this more when we consider van der Waals gas in more detail.

Example

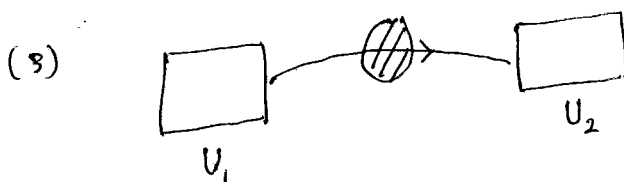
1 kg of water [Sp. ht = 1000 cal/kg] is heated by an electric stove from 20°C to 99°C (38)

Find

- (1) The change in internal energy
- (2) The change in entropy
- (3) Maximum work one can get using water at 99° as a heat reservoir and another sink at 20°

(1)  $\Delta U = Mc(99-20) = 1 \times 1000 \times 79 = 7.9 \times 10^4 \text{ cal.}$

(2)  $\Delta S = mc \int_{20}^{99} \frac{dT}{T} = 1000 \ln \frac{99+273}{20+273} = 1000 \ln \frac{372}{293} = 238.7 \text{ Cal/K}$



To do this think of running a Carnot engine between the 1 kg of water at 99° and the sink at 10°. Since the water at 99° is not an infinite reservoir, its temperature will decrease when it is at temperature T and in a cycle loses its temperature is T-dT then the heat supplied to the working substance is McdT. W.D for the reversible cycle is  $(1 - \frac{T_1}{T}) McdT = \Delta W$

Total work done =  $Mc \int_{20}^{99} (1 - \frac{T_1}{T}) dT = Mc(T_2 - T_1) - T_1 Mc \ln \frac{T_2}{T_1}$

$= 7.9 \times 10^4 - 293 \times 238.7 = 9066 \text{ Cal.}$