

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

$$\therefore \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial P} \right)_T$$

Using maxwell eqn again

$$\rightarrow \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

Using that -1 PD formula

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P}$$

another one of Maxwell's equations.

29th Feb 2024

Energy dimensions $\rightarrow u - pV + TS \rightarrow$ Infinite possibilities of constructing these.

But there are only specific constructions that are useful.

$$\rightarrow \text{Enthalpy} = H = u + pV$$

$$\rightarrow \text{Helmholtz free energy} = A(\text{chem}) = F = u - TS$$

$$\rightarrow \text{Gibbs free energy} = G = H - TS$$

$$\rightarrow \text{Internal energy} = u$$

There are combinations of state variables (out of inf possible)
Then why these 4?

o First ~~law~~ law: Energy conservation.

o Second law: Entropy increases for natural processes

Question: Will the processes in which entropy increases, ~~never~~ necessarily happen?

The ~~ans~~ answer to this dictated by thermodynamic potentials like H , F , G .

\Rightarrow Thermodynamic potentials minimized at eq.

Which ~~of~~ one of the potentials is relevant? It depends on the processes that we study.

Thus these determine if the processes can happen or not.

o $du = Tds - pdv$

$\Rightarrow u = u(s, v)$

$\therefore du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv$

$\Rightarrow T = \left(\frac{\partial u}{\partial s}\right)_v$, $P = - \left(\frac{\partial u}{\partial v}\right)_s$

$\Rightarrow \boxed{\left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v}$ \swarrow RHS become equal.

One of Maxwell's relations

Now,

$\frac{P}{T} = - \left(\frac{\partial S}{\partial v}\right)_u$ using

$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

Isobaric process: $du = Tds = \delta Q$

$$C_v = \left(\frac{\delta Q}{dT} \right)_v = \left(\frac{\partial u}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v$$

o Enthalpy: $H = u + pv$

$$dH = du + p dv + v dp$$

$$\Rightarrow dH = Tds - p dv + p dv + v dp$$

$$\Rightarrow \boxed{dH = Tds + v dp}$$

$$\Rightarrow H = H(S, P)$$

$$\therefore dH = \left(\frac{\partial H}{\partial S} \right)_P dS + \left(\frac{\partial H}{\partial P} \right)_S dP$$

Comparing,

$$T = \left(\frac{\partial H}{\partial S} \right)_P, \quad v = \left(\frac{\partial H}{\partial P} \right)_S$$

Using same method,

$$\boxed{\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial v}{\partial S} \right)_P} \quad \text{2nd Maxwell's relation.}$$

o Isobaric process: (most chem experiments)

$$dH = Tds = \delta Q = C_p dT.$$

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

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

Helmholtz free energy

$$F = U - TS$$

$$\rightarrow dF = -SdT - pdv$$

$$F = F(T, V)$$

$$\Rightarrow S = - \left(\frac{\partial F}{\partial T} \right)_V \quad , \quad p = - \left(\frac{\partial F}{\partial V} \right)_T$$

In Stat mech, we will derive expression for F for microscopic physics.

You get the third Maxwell relation from this, same method,

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

Consider a system going $i \rightarrow f$, s.t system is temp is constant.

↪ External condition (like ext press in chem)

In practice, it is like it is in touch with a reservoir.

$$\int_i^f \frac{dQ}{T} \leq S_f - S_i$$

$$\Rightarrow \int_i^f dQ \leq T(S_f - S_i)$$

$$\Rightarrow \Delta Q \leq TS_f - TS_i$$

o Question: work done by the system?

$$\Delta U = \Delta Q + \Delta W$$

↙ Sign
 $\Delta U = \Delta Q - |\Delta W|$

$$\Rightarrow \Delta U + |\Delta W| \leq TS_f - TS_i$$

$$\Rightarrow U_f - U_i + |\Delta W| \leq TS_f - TS_i$$

$$\Rightarrow |\Delta W| \leq [U_i - TS_i] - [U_f - TS_f]$$

$$\Rightarrow \boxed{|\Delta W| \leq F_i - F_f = -\Delta F}$$

ΔW for isothermal process has upper limit \rightarrow decrease in Helmholtz free energy.

7th March 2024

Thermodynamic systems find their equilibrium points at minimization of thermodynamic potentials

⊗ The thermodynamic potentials are related by Legendre transformations.

Using $du = Tds - pdv$ and each of the thermodynamic potentials, we can derive all of Maxwell's relations.

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

$$C_v \equiv \left(\frac{dQ}{dT}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v$$

$H = u + pv \rightarrow$ Thermo pots are func. of only state variables.

$$\Rightarrow dH = Tds + vdp$$

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p$$

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

$F = U - TS \rightarrow$ Helmholtz free energy.
(A in chem)

$$\Rightarrow dF = -SdT - pdv$$

$$\Rightarrow \left(\frac{\partial S}{\partial v}\right)_T = + \left(\frac{\partial p}{\partial T}\right)_v$$

↓
Arbeiter 'work'

When $dT=0$ (isothermal), $dF = -pdv \rightarrow$ work done.

$$\Rightarrow \Delta F = - \int p dv$$

(Isothermal)

→ Used a lot in physics.

* Calculation of internal states — important in Stat Mech. It is similar to how quantum mechanical states are fixed for fixed dimensions

$G = H - TS \rightarrow$ Gibbs free energy.

$$\Rightarrow dG = -SdT + vdp$$

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

Good for isothermal and isobaric

Helmholtz free energy →

Consider work done by the system →

$$\Delta U = \Delta Q \rightarrow \Delta W$$

$$\Rightarrow \Delta W = \Delta Q - \Delta U$$

Clausius → $\int_i^f \frac{dQ}{T} \leq S_f - S_i$

We take isothermal change from i to f .

$$\Delta Q = \int_i^f dQ \leq T(s_f - s_i)$$

$$\Rightarrow \Delta Q = \Delta U + \Delta W \leq T(s_f - s_i)$$

$$\Rightarrow U_f - U_i + \Delta W \leq T(s_f - s_i)$$

$$\Rightarrow \Delta W \leq [U_i - TS_i] - [U_f - TS_f]$$

$$\Rightarrow \boxed{\Delta W \leq -\Delta F}$$

Equality holds for reversible processes.

In the isothermal process, the work done by system can be at max change in Helmholtz free energy.

(reduction)

$$\therefore U = F + TS$$

accessible to U to do work

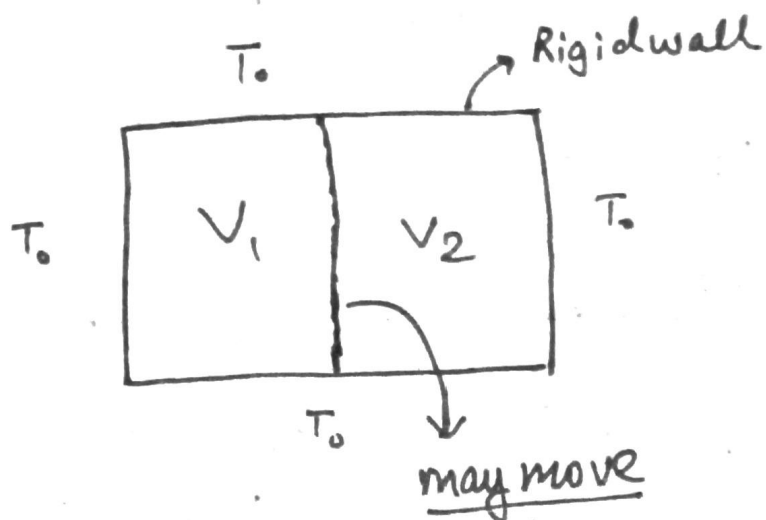
Not accessible to do work

Under isothermal process.

Consider isothermal and isochoric process.

$$0 \leq -\Delta F \Rightarrow F_f \leq F_i$$

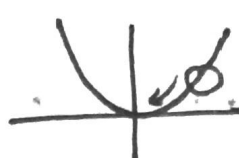
Why? Let us take an example.



$$V = V_1 + V_2$$

moves such the pressure on RHS and LHS are same.

How do we know this?

Using $F_f \leq F_i$, every step we take here (every movement of the wall), F ~~is~~ reduced. So, like SHO  $\rightarrow F$ is minimized.

$$F = F_1(V_1, T) + F_2(V_2, T)$$

$$\Rightarrow \delta F = \left(\frac{\partial F_1}{\partial V_1} \right)_T \delta V_1 + \left(\frac{\partial F_2}{\partial V_2} \right)_T \delta V_2$$

$$V = V_1 + V_2 = \text{constant}$$

$$\Rightarrow \delta V_1 = -\delta V_2$$

$$\therefore \left[\left(\frac{\partial F_1}{\partial V_1} \right)_T - \left(\frac{\partial F_2}{\partial V_2} \right)_T \right] \delta V_1 = \delta F = 0$$

\downarrow
 minima
 'extremized'

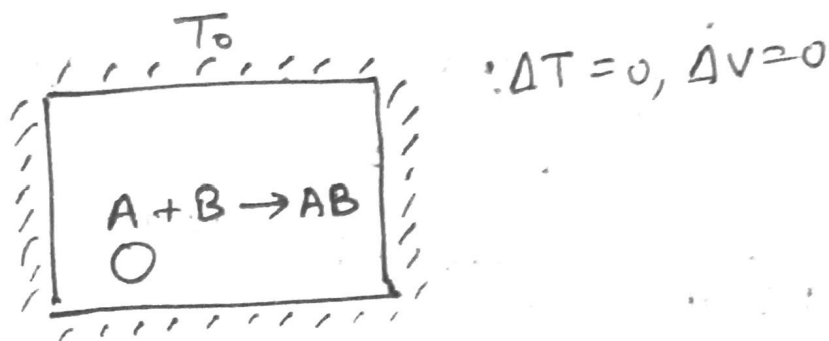
This can only hold if,

$$\left(\frac{\partial F_1}{\partial V_1} \right)_T = \left(\frac{\partial F_2}{\partial V_2} \right)_T \quad (\text{As } \delta V_i \text{ is arbitrary})$$

$$\Rightarrow P_1 = P_2 \quad (\text{Using Maxwell's relation})$$

Therefore, F is minimized: (This argument says extremized, but we can show that it is minimized) \square How?

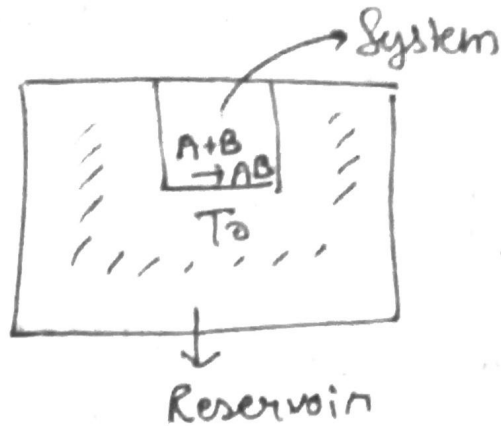
Similarly, if we take a chem reaction in isochoric + isothermal conditions,



Reaction will continue till F is minimized.

8th March 2024

$$dQ = -SdT + Vdp$$

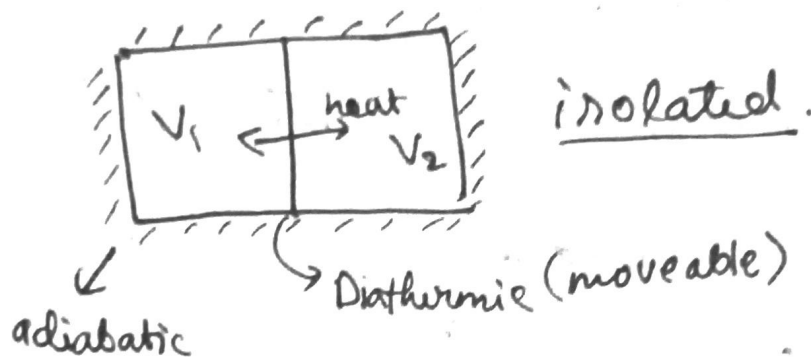


$$\Delta T = 0, \Delta V = 0$$

Some reaction
(chemical, ice melting
etc)
inside system - that is

where the heat energy is used.
Here F is minimized.

o Mechanical Equilibrium \rightarrow



At equilibrium, S is maximum.

$$\Rightarrow dS = 0 \text{ at equilibrium.}$$

Also,

$$U_1 + U_2 = U = \text{constant} \Rightarrow dU_1 = -dU_2$$

$$V_1 + V_2 = V = \text{constant} \Rightarrow dV_1 = -dV_2$$

$$dS = \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} dV_1 + \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1} dU_1$$

$$+ \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2} dV_2 + \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2} dU_2$$

$$\Rightarrow dS = \left[\left(\frac{\partial S_1}{\partial V_1} \right)_{U_1} - \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2} \right] dV_1$$

$$+ \left[\left(\frac{\partial S_1}{\partial u_1} \right)_{V_1} - \left(\frac{\partial S_2}{\partial u_2} \right)_{V_2} \right] du_1$$

$$\Rightarrow dS = du_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dv_1$$

$$= 0 \quad \text{As } S \text{ is maximum.}$$

$$\therefore \frac{1}{T_1} - \frac{1}{T_2} \Rightarrow \boxed{T_1 = T_2}$$

$$\frac{P_1}{T_1} - \frac{P_2}{T_2} \Rightarrow \boxed{P_1 = P_2}$$

Conditions req
for system to be in
thermodynamic
equilibrium.

□ Verify that second order
change of S is -ve — i.e. it is a maxima.

○ Thermodynamic relations with heat capacities:

$$S = S(T, V)$$

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

$$\Rightarrow \left(\frac{\partial S}{\partial T} \right)_P = \left(\frac{\partial S}{\partial T} \right)_V + \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

~~\Rightarrow~~

$$\Rightarrow T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow C_P - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P$$

$$= T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V \quad \text{Maxwell}$$

Easily measurable
quantities.

(observables)

Using any equation of state of we may derive $C_p - C_v$ using this.

Using the three derivative multiplied = -1 formula,

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

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

for normal materials, $\left(\frac{\partial P}{\partial V} \right) = -ve$

$$C_p > C_v \quad \text{usually.}$$

Now,

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

$$\Rightarrow \frac{\partial}{\partial T} \left[\left(\frac{\partial S}{\partial V} \right)_T \right] = \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

$$\Rightarrow \frac{\partial}{\partial V} \left[\left(\frac{\partial S}{\partial T} \right)_V \right] = \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V}$$

These are general and can be used with any eqn of state.

$$\left(\frac{\partial C_p}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

Same method
of derivation.

0 TdS equations →

$$S = S(T, V)$$

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

$$\Rightarrow TdS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$\Rightarrow TdS = C_V dT - T \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P dV$$

$$\Rightarrow \boxed{TdS = C_V dT + T \alpha E_T dV}$$

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ } \text{vol exp. coefficient.}$$

$$E_T = -V \left(\frac{\partial P}{\partial V} \right)_T \text{ } \text{isothermal elasticity.}$$

1st TdS equation

(There are 2 other)

2nd TdS equation:

$$TdS = C_p dT - TV \alpha dp$$

3rd TdS equation:

$$TdS = C_V \left(\frac{\partial T}{\partial P} \right)_V dp + C_p \left(\frac{\partial T}{\partial V} \right)_P dV$$

2 1/2 weeks of no classes.