Thermodynamics

Thermal Physics →
- Heat { Equilibrium, Steady state, non Equilibrium.
- K.T.
- T.D.
- Stat Mech. { Statistical T.D.

Useful Mathematical Tools

(a) Partial differentiation : $\frac{\partial f(a_1, a_2, \cdots, a_n)}{\partial a_1}$ $a_1, \cdots, a_n$ = independent variables.

Let $z = f(x,y)$ is an explicit function (surface plot in XYZ plane)

Motion of a coordinate point on the surface → 3 choices (i) x = constant y varies (ii) x varies y = constant, (iii) both x, y varies.

$x \rightarrow x + dx$, y = constant, $z = f(x+dx, y)$ from $f(x,y)$.

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{dx \to 0} \frac{f(x+dx) - f(x)}{dx} = f_x$$

Similarly $f_y = \left(\frac{\partial f}{\partial y}\right)_x = \lim_{dy \to 0} \frac{f(x, y+dy) - f(x,y)}{dy}$

& higher order derivates. $f_{xx} = \frac{\partial^2 f}{\partial x^2}$, $f_{xy} = f_{yx} = \frac{\partial^2 f}{\partial x \partial y}$ etc.

(b) Total differentials :

Let $z = f(x,y)$ an explicit function where, x, y are independent. means $dz \to 0$ implies $dx \to 0$ & $dy \to 0$ independently. Then

dz is the total differential $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$.

If an implicit function, say $f(x,y,z) = 0$ then

$$df = 0 = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = f_x dx + f_y dy + f_z dz$$

If $dx = 0$, $\left(\frac{\partial y}{\partial z}\right)_x = -\frac{f_z}{f_y}$, If $dy = 0$, $\left(\frac{\partial z}{\partial x}\right)_y = -\frac{f_x}{f_z}$ &

If $dz = 0$, $\left(\frac{\partial x}{\partial y}\right)_z = -\frac{f_y}{f_x}$. $\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$.

Also $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = M dx + N dy$ is perfect differential

if $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$.

Example Equation of state for hydrostatic system $f(P,V,T)=0$

substitute the variables, $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (volume expansivity)

$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ (isothermal compressibility)

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = +\frac{1}{KV}\beta V = \frac{\beta}{K}.$$

Get ~~back~~ the ~~same~~ expression $P = P(V,T)$

$$\text{or } dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT = -\frac{1}{KV}dV + \frac{\beta}{K}dT.$$

(c) Line integral & exact differential :

$dz = M\,dx + N\,dy \rightarrow$ required $z(x,y)$ at (x_1,y_1) & (x_2,y_2)

means $\int_{x_1}^{x_2} M(x,y)\,dx$, $\int_{y_1}^{y_2} N(x,y)\,dy$ be evaluated, provided

$y = f(x)$ dependency is given, meaning path in XY plane is given.

path dependent integration !! Each $f(x)$ gives different result.

However if dz is total differential, then

$$M = \frac{\partial z}{\partial x}, \quad N = \frac{\partial z}{\partial y} \quad \Rightarrow \quad \frac{\partial M}{\partial y} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial N}{\partial x}$$

From this we can evaluate z by $\int_x\int_y$ without using $y=f(x)$

path independent integration !!

It only depends on (x_1,y_1) & (x_2,y_2) ; z is called "point function".

If contour integral over complete cycle $\oint dz = 0$ if dz is exact or total differential.

Change of state of a system may be of different types:

Isothermal (diathermic): If the change of state is such that the temperature of the system remains constant, then that state is called isothermal (T = constant).

Isobaric: If the process is such that the pressure remains constant then it is called isobaric (P = constant).

Isochoric: If during the change of state, the volume of the system does not change, then it is called isochoric (V = constant)

Adiabatic: If the change is such that there is no exchange of heat then it is called adiabatic (Q = constant)

Isentropic: If during the change, the entropy of the system remains constant, then it is called isentropic (S = constant)

Isenthalpic: If during the change of state, the total heat content remains constant, then it is called isenthalpic process ($H = U + PV$ = constant)

Thermodynamic System

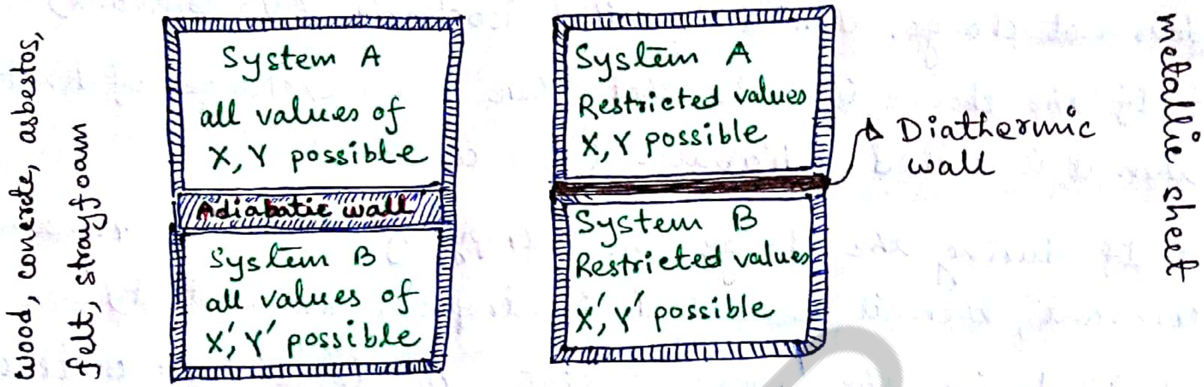
"System" refers to a certain portion of the universe within some closed surface (boundary). Boundary may enclose a solid, liquid, gas, collection of magnetic dipoles, portion of liquid surface, batch of radiant energy & so forth. Boundary is not necessarily fixed in shape or size & can be real or imaginary. Like inner surface of tank (real) containing a compressed gas or surface enclosing certain mass of fluid (imaginary).

Many problems involve interchange of energy between a given system & others. Such other systems that can interchange energy with the system are called "surroundings". System & surrounding together constitute the universe.

When conditions are such that no energy interchange with the surroundings can take place, then the system is said to be "isolated". If no matter can cross the boundary, then its a "closed" system. But if interchange of matter between system & surrounding, then its an "open" system.

Thermal Equilibrium

Consider a system having two independent coordinates X, Y (say pressure, volume or temperature). A state of the system in which X & Y have definite values that remain constant as long the external conditions are not changed is called an equilibrium state. Such equilibrium state in a system depends on the proximity of other systems & also on the nature of the separating wall.

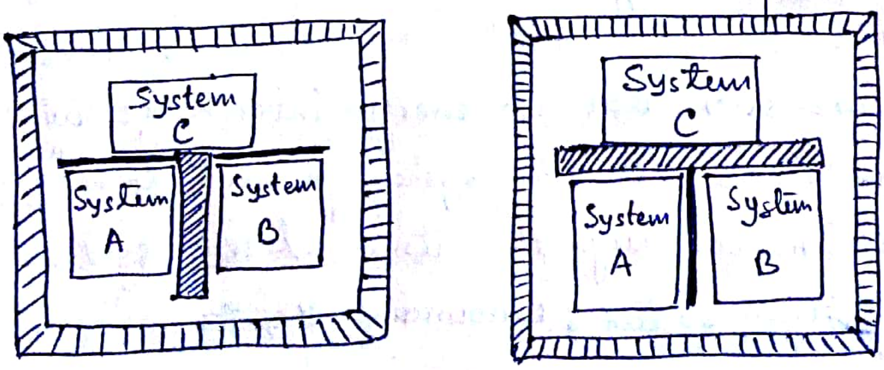


For adiabatic wall, state X, Y for system A may coexist with state X', Y' of system B as equilibrium state. But for diathermic wall, (X, Y) & (X', Y') will change spontaneously until an equilibrium state of the combined system is attained.

Zeroth law of Thermodynamics (Fowler, 1908)

If two system A & B separated by an adiabatic wall but each of them are in contact with a third system C through diathermic wall, then A & B will come to equilibrium with C & no further change will occur if the adiabatic wall between A & B is replaced by diathermic wall.

0^{th} law of T. D. : 2 systems in thermal equilibrium with third are in thermal equilibrium with each other.



Thermodynamic equilibrium

A system is said to be in a state of thermodynamic equilibrium if (a) mechanical equilibrium, (b) chemical equilibrium & (c) thermal equilibrium is satisfied.

When there is no unbalanced force in the interior of a system & also no net force between a system & its surrounding (also net torque is zero), then the system is in a state of mechanical equilibrium.

When a system in mechanical equilibrium does not undergo a spontaneous change in its internal structure (e.g. chemical reaction) mass transfer due to diffusion) then the system is in a state of chemical equilibrium.

Thermal equilibrium exists when there is no spontaneous change in the (thermodynamic) coordinates (e.g. P, V, T) of a system in mechanical & chemical equilibrium when separated from surroundings by diathermic wall.

Non equilibrium states cannot be described in terms of T.D. coordinates as $P = P(x, y, z)$ that varies in space & time.

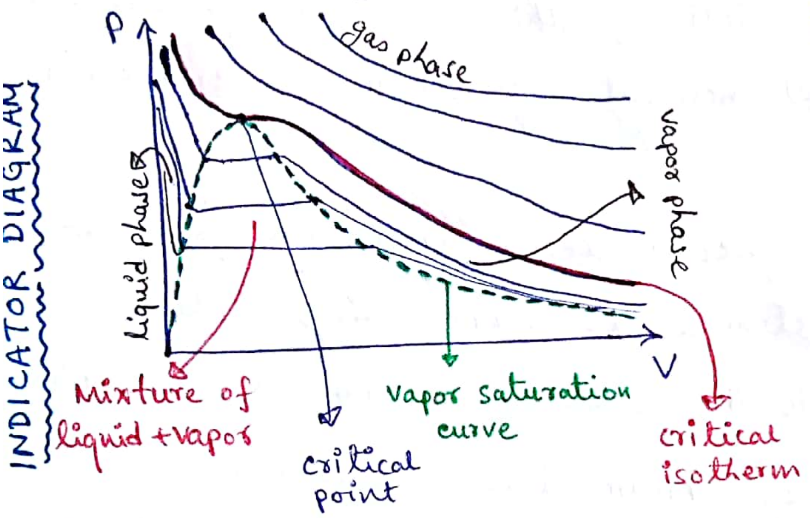
In the absence of surface, gravitational, electric, magnetic effects a constant mass system that exerts uniform hydrostatic pressure to surroundings is a "hydrostatic system". Categorically 3 systems:

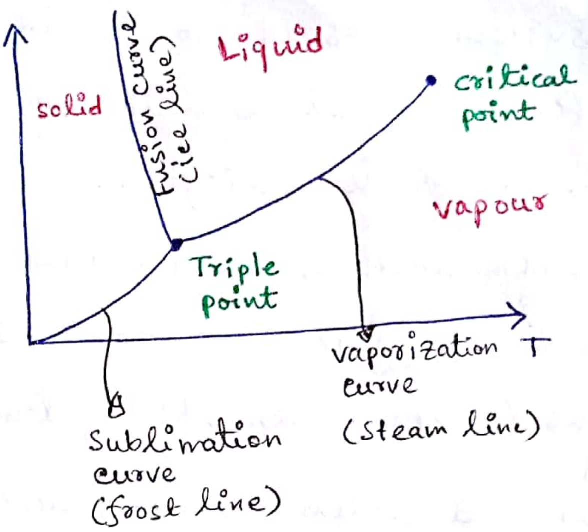
1. A pure substance : 1 chemical constituent (solid, liquid, gas) mixture (s-l, l-g, s-g) or three of them (s-l-g).

2. Homogeneous mixture of different constituents : mixture of inert gases, mixture of liquids (solution)

3. Heterogeneous mixture : mixture of different gases in contact with a mixture of different liquids.

PV & PT diagram for pure substance





Thermodynamic description of system other than $f(P,V,T)=0$

Thermodynamics of a gaseous system is described by three thermodynamic coordinates P, V, T, but for other systems require different types of coordinates.

Stretched Wire $P, V \sim$ unchanged. Thermodynamicall equivalent coordinates (a) Tension in the wire ($\mathcal{F}$), (b) Length of the wire (L) (c) Ideal gas temperature (T). In S.I. units, $\mathcal{F}$ is Newton, L is metre, T in °K.

Equivalent of equation of state $f(P,V,T)=0$ is the Hooke's law at constant temperature within elastic limit.

$$\mathcal{F} = K(L - L_0) \quad , \quad L_0 = \text{length at no tension}$$

So, $L = L(\mathcal{F}, T)$ & for infinitesimal change

$$\therefore \; dL = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F} + \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} dT$$

Linear expansivity $\alpha = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}}$

Isothermal Young's modulus $Y = \left(\frac{\partial \mathcal{F}/A}{\partial L/L}\right)_T = \frac{L}{A}\left(\frac{\partial \mathcal{F}}{\partial L}\right)_T$

$$\therefore \; dL = \frac{L}{AY} d\mathcal{F} + \alpha L \, dT.$$

For isothermal condition $d\mathcal{T} \simeq 0$ & $dL = \frac{L}{AY} d\mathcal{F}$ &

therefore work done in expanding a wire is

$$W = \int \mathcal{F} \, dL = \int_0^{\mathcal{F}} \mathcal{F} \frac{L}{AY} d\mathcal{F} = \frac{L}{2AY} \mathcal{F}^2.$$

Surface film

physical chemistry / chemical engineering / other areas.

Examples (a) Liquid-vapour interface in equilibrium,
(b) soap bubble / film → two surface films with in between liquid,
(c) thin oil film on the surface of water.

Three coordinates (a) surface tension $\mathcal{S}$ (Newton/metre), (b) area of film (A) metre^2, (c) ideal-gas temperature T. to describe a stretched membrane.

Equation of state $\mathcal{S} = \mathcal{S}_0 \left(1 - \frac{T}{T'}\right)^n$ for surface tension

$\mathcal{S}_0$ = surface tension at 0°c, $T' \sim$ near T_c & $n \sim 1$ & 2.

As T >, $\mathcal{S}$ < & = 0 at $T = T'$.

Dielectric slab

Thermodynamic behaviour of a dielectric slab (whether molecules are polar or nonpolar) is described by three coordinates, (a) electric field intensity E (V/m), (b) electric polarisation (P) in Coulomb meter which is the amount of dipole moment per unit volume along the direction of the electric field.

The equation of state of the dielectric

$$P = \left(A + \frac{B}{T}\right) E$$ where A, B are constants & depends upon the nature of the dielectric material.

Paramagnetic Rod

When a paramagnetic rod is placed within a solenoid, where the magnetic intensity is H, the rod develops a magnetic moment M. Magnetic induction B in volume V is

$$B = \mu_0 \left(H + \frac{M}{V}\right).$$

Equivalent thermodynamic coordinates are (1) Magnetic field intensity H (Ampere/metre), (2) Magnetization M (Ampere metre^2), (3) Ideal gas temperature T. (in °K).

The equation of state of thermodynamic equilibrium is

$$M = C \frac{H}{T} \quad \text{(Curie's law)}$$

Intensive & Extensive Parameters

If a system in equilibrium is divided into two parts, each with equal mass, then those properties of each half of the system that remain same are called intensive & those which become half are called extensive.

Systems	Intensive coordinates	Extensive coordinates
(a) Hydrostatic system	Pressure (P)	volume (V)
(b) stretched wire	tension ($\mathcal{F}$)	Length (L)
(c) surface film	Surface tension ($\mathcal{S}$)	Area (A)
(d) Dielectric slab	Electric field Intensity (E)	Polarization (P)
(e) Paramagnetic rod	Magnetic field Intensity (H)	Magnetization (M)

Equation of state for adiabatic process

Let us consider an ideal gas system of volume V at pressure P. Then for isothermal change, $PV = \mu RT = \text{constant}$ (as T = constant)

Now for an adiabatic process without any exchange of heat, using first law of thermodynamics $0 = dU + PdV$.

where dU is the internal energy change & if the change in temperature for one mole of gas is dT, then $dU = C_V dT$

where C_V is the specific heat at constant volume.

$\therefore \quad C_v dT + P dV = 0$ for adiabatic process.

From equation of state $PV = RT \quad \therefore \quad PdV + VdP = RdT$

$\therefore \quad dT = \dfrac{PdV + VdP}{R} = \dfrac{PdV + VdP}{C_p - C_v}$ as $C_p - C_v = R$ for ideal gas.

$\therefore \quad C_v \left(\dfrac{PdV + VdP}{C_p - C_v} \right) + PdV = 0$

or $\dfrac{\cancel{C_v P dV} + C_v V dP + C_p P dV - \cancel{C_v P dV}}{C_p - C_v} = 0$ or $C_v V dP + C_p P dV = 0$

or $\dfrac{dP}{P} + \dfrac{C_p}{C_v} \dfrac{dV}{V} = 0$, integrating $\ln P + \gamma \ln V = \ln C$

$[\gamma = \frac{C_p}{C_v}, \ln C \text{ constant}]$

or $PV^{\gamma} = $ constant

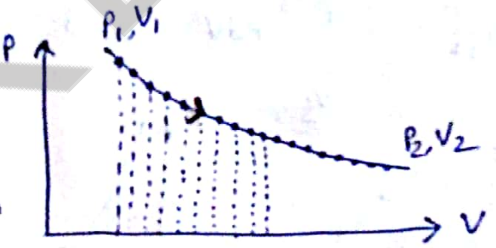
Using $PV = RT$ or $V = \dfrac{RT}{P} \Rightarrow P\left(\dfrac{RT}{P}\right)^{\gamma} = $ constant

or $P^{1-\gamma} T^{\gamma} = $ constant.

Again using $PV = RT$, $P = \dfrac{RT}{V} \Rightarrow \dfrac{RT}{V} V^{\gamma} = $ constant

or $V^{\gamma - 1} T = $ constant.

Quasistatic Process

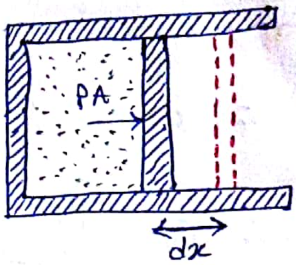


A finite unbalanced force may cause a system to pass through nonequilibrium states. Thus during a process if it is required to describe every state of the system by means of thermodynamic coordinates, the process should not conceive a finite unbalanced force, because a nonequilibrium state cannot be defined by thermodynamic coordinates. Therefore we think of an ideal situation in which external forces vary slightly so as the unbalanced force is infinitesimal. A process performed in such ideal way is "quasistatic." [In statmech course, rethink about "local equilibrium"]

During a quasistatic process the system is infinitesimally near a state of thermodynamic equilibrium, & all states through which the system passes can be described with equation of state with thermodynamic coordinates.

Work done "on" or "by" a system in a quasistatic process

(a) Gaseous hydrostatic System



pressure exerted by the system on piston = PA

opposing force on the system by external agent moves piston by dx in opposite direction to PA

($dV = Adx$)

Then $đW = -PAdx = -PdV$

If $dV > 0$ (expansion), $đW < 0$ (negative work)

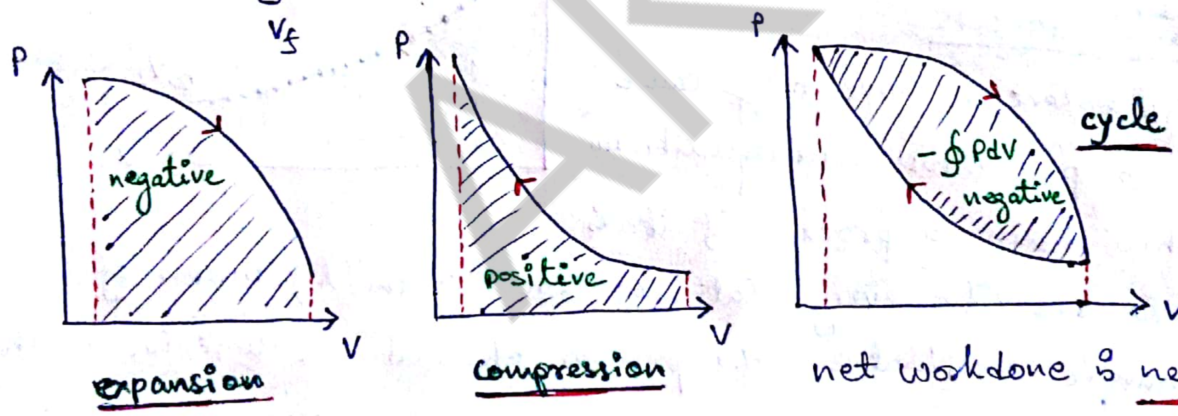
$dV < 0$ (compression), $đW > 0$ (positive work)

for finite quasistatic process $W = -\int_{V_i}^{V_f} PdV$

This depends on path because $P = P(T,V) \Rightarrow P = P(V)$ for given T.

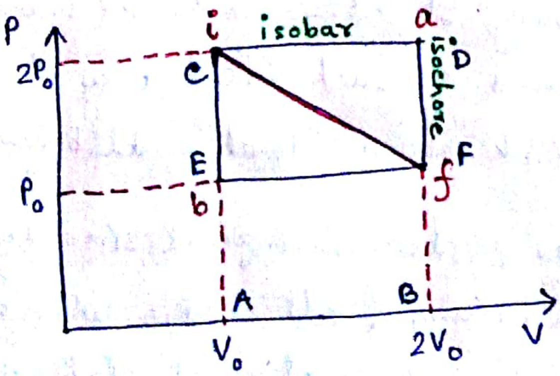
∴ Work done "on" a system from larger volume (V_i) to smaller volume (V_f) is $W_{if} = -\int_{V_i}^{V_f} PdV$ & for expansion, workdone "by" system is $W_{fi} = -\int_{V_f}^{V_i} PdV$ and when path is quasistatic, $W_{fi} = -W_{if}$

INDICATOR DIAGRAM



net workdone is negative

Path dependency: Exact & inexact differentials



Many route to go from $i \rightarrow f$.

(a) $i \rightarrow a$ (isobaric) $\Rightarrow$ $a \rightarrow f$ (isochoric)

$$W.D. = \underbrace{-\int PdV}_{\text{area ABDC}} = -2P_0V_0$$

(b) $i \rightarrow b$ (isochoric) $\Rightarrow$ $b \rightarrow f$ (isobar)

$$W.D. = \underbrace{-\int PdV}_{\text{area ABFE}} = -P_0V_0$$

(c) $i \to f$, W.D. $= -\int_{\text{area ABFC}} PdV = -\int_{\text{area ABEF}} PdV - \int_{\text{area EFC}} PdV = -\frac{3}{2}P_0V_0$

Infinitesimal amount of work is "inexact differential", means it is not the differential of a function of thermodynamic coordinates. That's represented with $đW$, & it depends on the path.

Suppose if functional differential $df = 2xy^3dx + 3x^2y^2dy$
$= d(x^2y^3)$.

$\int_{x=y=1}^{x=y=3} df$ depends only on the limit & not on path. df is an "exact differential."

Isothermal quasistatic expansion/compression

Using $PV = nRT$, $W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT\ln\frac{V_f}{V_i}$

$n = 2$ kmol, $T = 273K$ ($0^\circ C$), $R = 8.31$ kJ/kmol.K, $V_i = 4m^3$, $V_f = 1m^3$ (compression), $W = 6300$ kJ = positive work (work done "on" gas)

Isothermal quasistatic increase of pressure on solid

$V = V(P,T)$ $\therefore dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT = \left(\frac{\partial V}{\partial P}\right)_T dP$ (isothermal)

isothermal compressibility $= \frac{1}{\text{bulk modulus}} = \frac{1}{dP/(\frac{dV}{V})}$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$\therefore dV = -\kappa V dP$

So Work done $= \int_{P_i}^{P_f} P\kappa V dP \approx \frac{\kappa V}{2}(P_f^2 - P_i^2) = \frac{\kappa m}{2\rho}(P_f^2 - P_i^2)$

for copper, at $T = 273K$, $\rho = 8930$ Kg/m^3, $\kappa = 7.16 \times 10^{-12}$ Pa^{-1}, $m = 100$ kg, $P_i = 0$, $P_f = 1000$ atm $= 1.013 \times 10^8$ Pa

$W = 0.411$ KJ. = positive work (work done "on" copper)

(b) Isothermal stretching a wire

If tension $\mathcal{F}$ changes length of wire from L to $L+dL$ (extension) then work done on the wire (positive work) is

$$W = \int_{L_i}^{L_f} \mathcal{F}\, dL$$

remember, $L = L(\mathcal{F}, T)$ & for isothermal

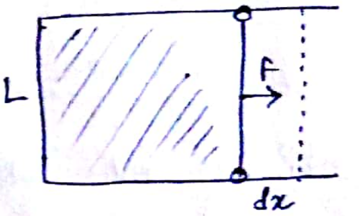
$$dL = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F} + \left(\frac{\partial L}{\partial T}\right)_{\mathcal{F}} dT = \left(\frac{\partial L}{\partial \mathcal{F}}\right)_T d\mathcal{F}$$

$$= \frac{L}{AY}\, d\mathcal{F} \quad \text{using "isothermal Youngs modulus"}$$

$$= \int_0^{\mathcal{F}} \frac{L}{AY} \mathcal{F}\, d\mathcal{F}$$

$$= \frac{L}{2AY} \mathcal{F}^2.$$

(c) Surface film



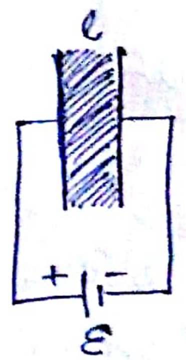
If γ is surface tension of a double surface film with liquid in between then force exerted on both film is $2\gamma L$ & for displacement dx, work done "on" the film (positive)

$$dW = 2\gamma L\, dx = \gamma\, dA \qquad (\text{as } dA = 2L\,dx)$$

$$\therefore W = \int_{A_i}^{A_f} \gamma\, dA$$

[For soap bubble $A = 2 \times 4\pi R^2$, $W = 8\pi\gamma R^2$]

(d) Polarization of a dielectric solid



Consider a slab of isotropic dielectric material between conducting plates of a parallel-plate capacitor, with area A & separation l connected to a battery to yield potential difference $\mathcal{E}$.

Uniform field intensity $E = \dfrac{\mathcal{E}}{l}$.

work done against the electric field to move dZ amount of charge

$$\text{is } dW = \mathcal{E}\, dZ = E l\, dZ = E l A\, dD$$
$$= E V\, dD$$

[as $Z = DA$ = total charge & D = electric displacement]

[as $V = lA$]

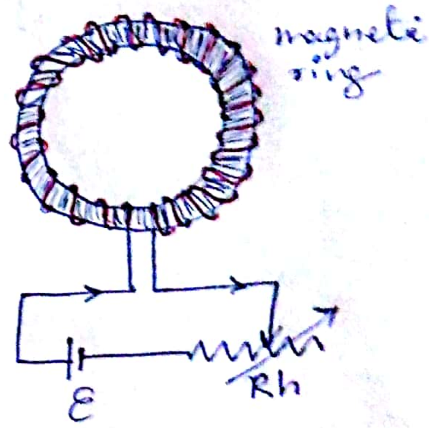
Now $D = \epsilon E = \epsilon_0 E + \dfrac{P}{V}$

$\therefore \; dD = (\epsilon_0 dE + \frac{dP}{V})$ & then

$$dW = EV(\epsilon_0 dE + \frac{dP}{V}) = \underbrace{V\epsilon_0 E dE}_{[vacuum]} + \underbrace{E dP}_{[material]}$$

$\therefore$ Net work on dielectric is $dW = E dP$, $W = \int_{P_i}^{P_f} E dP$

(e) Magnetization of a magnetic solid



magnetic ring cross sectional area A, circumference L. Insulated wire is wind on that (Toroidal winding)

Current in the winding initiate magnetic field with induction B (uniform). Using Rheostat if current is changed in time dt then

$$\mathcal{E} = -NA\frac{dB}{dt} \quad \text{(Faraday's principle of EM induction)}$$

N = number of turns and $H = ni = \frac{Ni}{L} = \frac{NAi}{V}$ $(V = AL)$

If dZ charge is transferred in circuit, work done "by" system to maintain current is $dW = -\mathcal{E}\, dZ = NA\frac{dB}{dt} dZ$

$$= NA\frac{dZ}{dt} dB = NAi\, dB$$

$$= VH\, dB.$$

If M = total magnetic moment, then

$$B = \mu H = \mu_0 H + \mu_0 \frac{M}{V} \Rightarrow dB = \mu_0 dH + \mu_0 \frac{dM}{V}$$

$$\therefore \; dW = \underbrace{V\mu_0 H dH}_{[vacuum]} + \underbrace{\mu_0 H dM}_{[material]}$$

Work done to change the magnetization is $dW = \mu_0 H dM$

or $W = \mu_0 \int_{M_i}^{M_f} H dM$.

$$\boxed{\text{Work (extensive)} = \text{Intensive quantity} \times \text{Extensive quantity}}$$