LECTURE NOTES ON PHS 222 (THERMAL PHYSICS)

BY

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PHS 222: THERMAL PHYSICS

CONTENT

- Heat Energy; Conduction, Convection, Radiation
- Zeroth Law of Thermodynamics and temperature definition.
- The first Law (of thermodynamics) :- Work, Heat, internal Energy.
- Carnot cycle and the second Law:- Entropy and irreversibility.
- Thermodynamics potential
- Quantitative discussion of phase transitions.
- Elementary kinetic theory of gases; Boltzmann counting, Maxwell-Boltzmann Law of distribution of velocities, simple applications.

Heat Energy

What is Energy? This is capacity of matter to perform work as a result of its motion or position in relation to forces acting on it. In other words, if you move a load "*Mg*" through a distance "*h*" you then have done a work *Mgh*!

Energy associated with motion is known as kinetic energy; while energy associated with position is known as potential energy.

Energy exists in various forms: mechanical, thermal, chemical, radiant, atomic, etc. Thermal energy therefore, is the energy derived from heat.

Heat can be transferred in various forms/ways such as conduction, convection and radiation.

CONDUCTION

Conduction can only take place if there is difference in temperatures. It occurs through free e-s (thermal agitation)

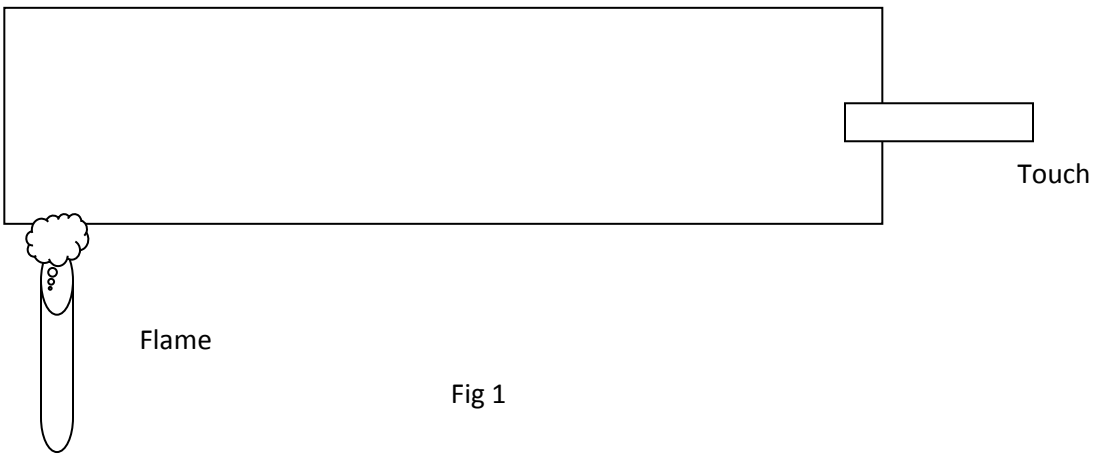


Fig 1

Consider a material of cross section *A* and thickness *L*

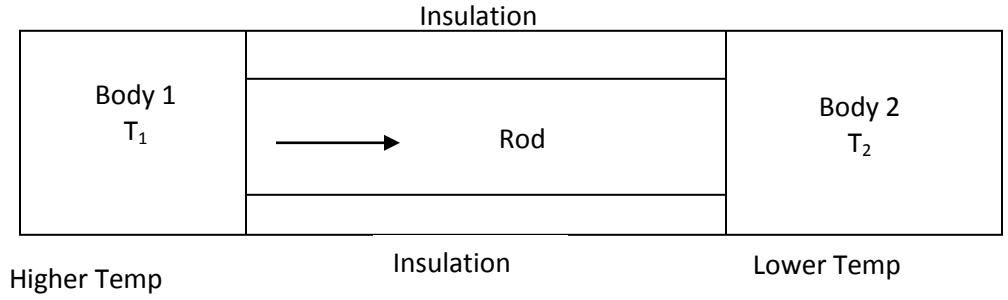


Fig 2

If body *1* is kept at temperature T_1, a higher temperature them body *2* at T_2, then the heat current will move from body *1* towards body 2. After a while, the temperature at points within the rod will be found to decrease uniformly with distance from the hot (Body 1) to the cold (Body 2) face. However, the temperature remains constant with time at each point. This is the so called steady- state heat flow.

The rate of flow of heat through the rod in the steady state is proportional to the area, the thickness of the rod and temperature difference: i.e.

$$H \alpha A \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

$$H \alpha {}^{1}/_{L} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

$$H \alpha (T_1 - T_2) \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (3)$$

$$\therefore H = K \frac{A(T_1 - T_2)}{L} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (4)$$

Where,

K = thermal conductivity of the rod material.

Now, *H* is known as the quantity of heat flowing through the rod per unit time. It is also known as heat convent.

In a case of a thin layered material perpendicular to the direction of flow; if *x* is the coordinate along the flow path, Δx the thickness of the layer and *A* the cross sectional area perpendicular to that path then,

$$H = \frac{-KA\Delta T}{\Delta x} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (5)$$

Where,

Δx is the change in temperature. The negative sign is due to the fact that the temperature decreases in the direction of increasing x (note that Δx and ΔT are positive).

The direction of heat flow in the direction of decreasing x.

The quantity:

$\Delta T/\Delta x$ …… (6)

is known as temperature gradient.

S. I unit of rate of heat flow is Joule per second (J/s)

$\Rightarrow k = \frac{-H\Delta x}{A\Delta T} \equiv \frac{(1\text{J.s}^{-1})(1\text{m})}{(1\text{m})^2(1\text{C}^0)} \equiv J.(s.m.C^0)^{-1} \equiv W.m^{-1}K^{-1}$ ---------- (7)

CONVECTION

A process of heat transfer in which there is actual motion of material is known as convection. Some examples are: the hot air furnace, the hot-water heating system, flow of blood in the body system, Convection air current, boiling of water in pot (Conduction and Convection)

We can distinguish two types of convection :

(a) Forced convection: This is a process in which a material is forced to move by a blower or pump leading to transfer of heat.

(b) National or free convection:- this is a process in which a material flows due to differences in density.

Unlike in conduction, the heat equation convection is very complex, however if one defines a convection coefficient h, then.

$H = hA\Delta T$ …… *(8)*

Where H is the heat gained or lost by convection by a surface per unit time

A = Area of the surface

ΔT = Temperature difference.

RADIATION

The process whereby there is a continuous conversion of energy from the surface of a material is known as radiation. Thus radiant energy (electromagnetic waves) is emitted at the speed of light through vacuum and air. When radiant energy falls on an opaque material, it is absorbed by the material resulting in transfer of heat (to the material).

The radiant energy emitted by a surface per unit time and per unit area, depends on (1) the nature of the surface and (2) its temperature.

The rate of radiation at low temperature is small implying a relatively long wave length radiant energy. As temperature increases, the rate of radiation also increases in proportion to the fourth power in temperature; i.e.

$$H \propto T^4 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

Also, $$H \propto A \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

H depends on the nature of the surface described by a dimensionless number, *e*, which is between 0 and 1. Hence,

$H \propto e$, the emissivity ……..(11)

$\therefore H \propto A\, e\, T^4$ ……. (12)

$\Rightarrow\gg H = \sigma\, A\, e\, T^4$……. (13)

$\sigma$is a constant known as Stefan-Boltzmann constant

H has the units of power (energy per unit time) i.e. σ has units: $W.m^{-2}$, k^{-4} …….. (14)

The emissivity for dark, rough surfaces are higher than those for light, smooth surfaces.

If a body is completely surrounded by walls at a different temperature T_w, then the net rate of loss (or gain) of energy per unit area by radiation is:

$H_{net} = A\, e\, \sigma T_1^4 - A\, e\, \sigma T_w^4 = A\, e\, \sigma(T_1^4 - T_w^4)$ …….. (15)

Practice Question

1. A slab of a thermal insulator is $100cm^2$ in cross- section and 2cm thick. If it has a thermal conductivity of 0.1 $J.s^{-1}\ m^{-1}\ (C^0)^{-1}$, and a temperature difference of 100^0C between opposite faces; calculate the heat flow through the slab in a day.

2. A solid wood door has dimensions 2m x 0.8m x 4cm and a thermal conductivity *k* of 0.04 $J.S.^{-1}.m^{-1}(C^0)^{-1}$. The inside air temperature is 20^0C and the outside air temperature is -10^0C. What is the rate of heat flow through the door, assuming the surface temperature are those of the surrounding air?

3. A vertical steam pipe of outside diameter 7.5cm and height 4m has its outer surface at a constant temperature of 95^0C. The surrounding air is at atmospheric pressure and at 20^0C. How much heat is delivered to the air by natural convection in 1hour?

4. The emissivity of tungsten is approx. 0.35. A tungsten sphere 1cm in radius is suspended within a large evacuated enclosure whose walls are at 300k. What power input is required to maintain the sphere at a temperature of 3000K if heat condition along the supports is neglected?

Laws Of Thermodynamics

What is Thermodynamics?

Thermodynamics is the branch of physics that describes and correlates the physical properties of macroscopic systems of matter and energy. In other words, it is concerned with heat and related thermal phenomena. The various laws of thermodynamics enable us to accurately describe processes involved in heat energy.

The Zeroth Law: States that if two systems *A* and *B* are in thermal equilibrium with a third system *C,* then they are in equilibrium with each other i.e. *A* is in equilibrium with *C* or *B* is in equilibrium *C*. We can then determine the direction of heat flow when two systems (*A* and *B*) are put in contact. One system *A* is said to be hotter than another *B* if heat flows from the former (*A*) to the latter (*B*) when they are in thermal contact.

This then allows us to introduce a parameter, called an empirical temperature, which is the same for all bodies that are in thermal equilibrium with each other. This is done by constructing a system, called a thermometer which allows us to ascribe a number to the temperate.

The first law of Thermodynemics (Law of conservation of Energy)

The Law tells us that heat is a form of energy which is conserved. The 1st Law applies to closed systems, i.e for a given amount of matter, and is expressed in the form of an energy balance equation:

$du = dq + dw$ ----------16

The above equation states that a small change (*du*) in the internal energy (*u*) of a closed system is the sum of a small amount (*dq*) of heat supplied to the system and the work performed (*dw*)) on the system.

Note that, *dq* may be positive or negative and that *dw* can assume many different forms depending on the type of action to which the system is subjected.

Here we will assume work done to be

$dw = -P_{ext}\, dV$ ---------- 17

Where P_{ext} = external pressure applied in order to perform work, which causes a change in volume *dV*.

The negative sign implies compression ($dV<0$) when *dw* should be positive

Now equation *16* becomes

$du = dq - P_{ext}\, dV$ ---------- 18

$dV > 0$ *or* $dV < 0$ depending on whether the internal pressure, P_{int} of the system is higher or lower than P_{ext} respectively. In particular, if

$P_{ext} = P_{int} = P$ ---------- 19

Then the piston will not move spontaneously but may be displaced reversibly.

A reversible process is one that can be retraced completely without effecting any permanent change in the surroundings.

The quatities or variables *U, P,* and *V* are called functions of state or state variables. The absolute temperature *T* (in Kelvin) is also a function of state.

Functions of state can either be:

1. Extensive functions of state: These are those that are proportional to the size or qauntity of a system or substance; e.g. *U, V, n* (no. of moles).

2. Intensive functions of state: Those that are independent of system size: e.g. *T,P, V/n, U/n*

$V/n = \bar{V}$ = molar volume

$U/n = \bar{U}$ = molar energy.

For any substance that is uniform in composition and physical properties, then the macroscopic state of such system can be determined by specifying two intensive variables E.g. T and P: such that

$$\left.\begin{aligned} U &= U(T,P) = n\bar{U}(T,P) \\ V &= V(T,P) = n\bar{V}(T,P) \end{aligned}\right\} \text{---------- 20}$$

The equation of state of a system can therefore be written as :

$\frac{V}{n} = \bar{V} = \frac{RT}{P}$ (For ideal gas) ----------21

$(P + \frac{a}{\bar{V}^2})(\bar{V} - b) = RT$ (for real gas e.g. van der Waals)----------22

Where b is the effect of finite size of the molecule, $\frac{a}{\bar{V}^2}$ is the effect of the attractive (dispersion) forces. It follows that from the ideal gas model,

$\bar{U} = \bar{U}(T)$ ----------23

We can now write on equation of state in a *PV* – diagram where, for each *T*, the *P*-*V* relationship describes a curve, called an isotherm. The PV – diagram can also be used to represent a reversible change of a system. Each point *(V, P)* corresponds to definite values of both T and U.

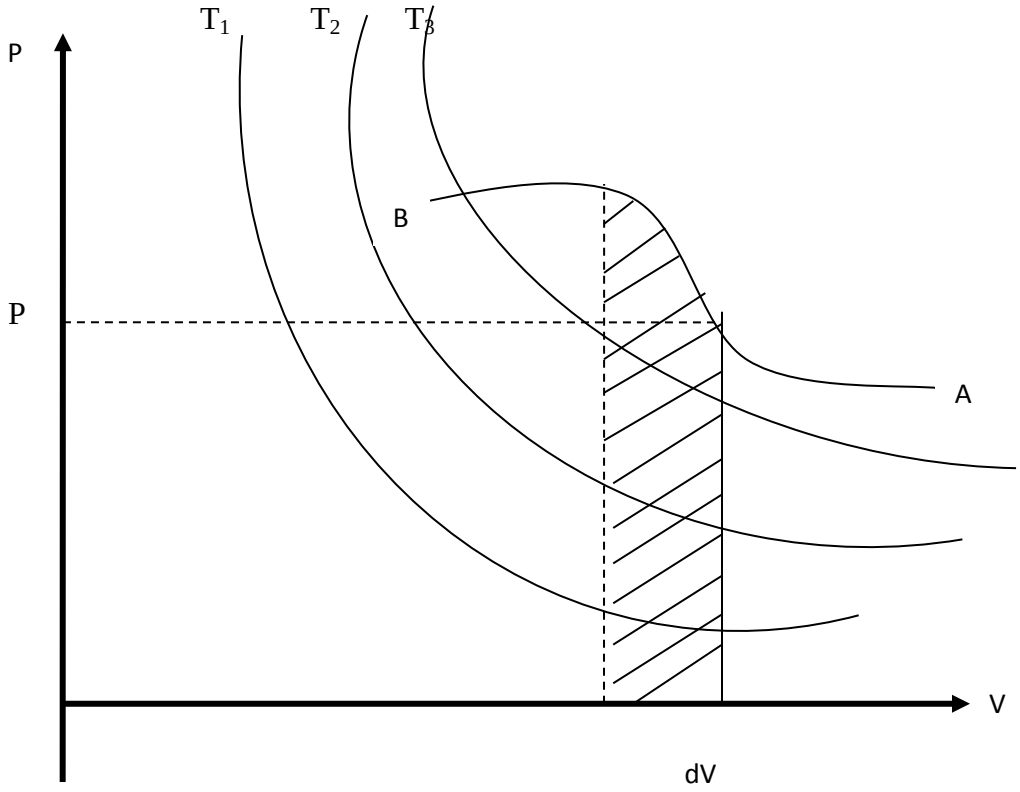


Figure 3

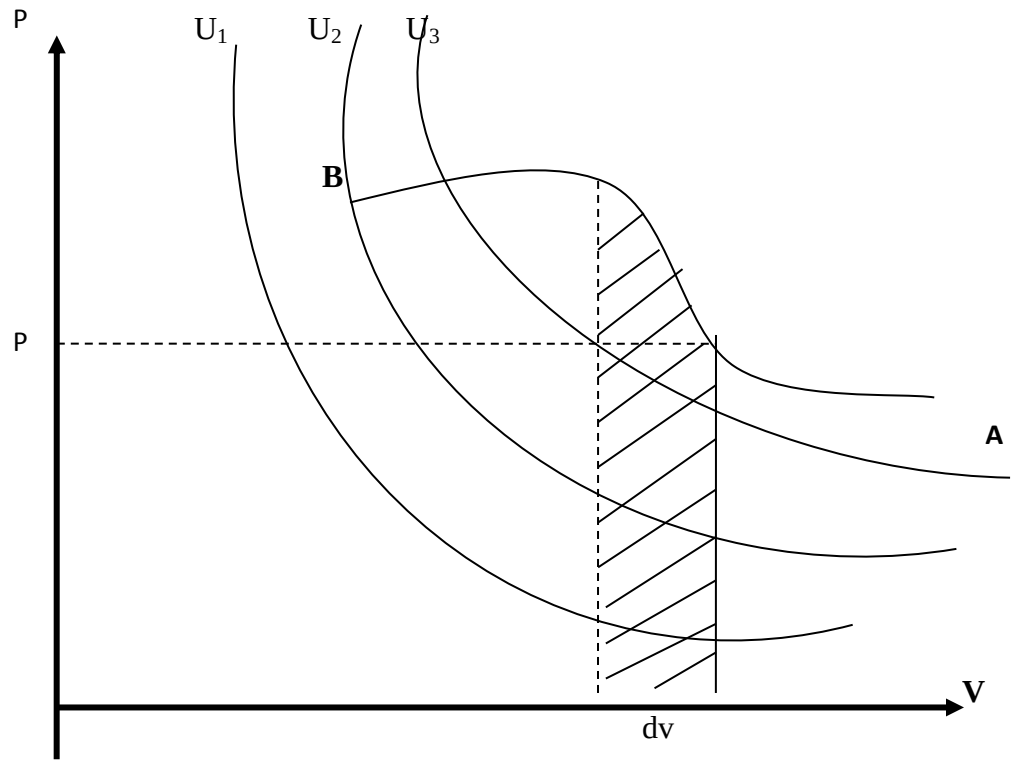


Figure 4

For a finite change of state, moving from A to B, the net amount of *PV* – work is equal to the area under the curve:

$W = \int_A^B dw_{rev.} = - \int_A^B Pdv = + \int_B^A Pdv$ ---------- (24)

We see that the value of W depends on the path leading from A to B, i.e. W is not a function of state.

Any change in U,

$\Delta U = U_B - U_A$ ---------- (25)

Depends only on the initial and final states, not on the path connecting them or upon whether the process is reversible or not. Then:

$\Delta U = q + W$ ---------- (26)

At constant pressure (where the piston is free to move),

and
$$\left.\begin{aligned} W &= -P\Delta V \\ \Delta U &= q - P\Delta V \end{aligned}\right\} \text{----------(27)}$$

Alternatively,

$$(\Delta H)p = q \quad [\ i.e.\ \ \Delta U + P\Delta V = \Delta H] \text{ ----------} \quad (28)$$

where H represents enthalpy or heat content. Obviously,

$$H = U + PV \text{ ----------} \quad (29)$$

We can define heat capacity *C* as;

$$C = \frac{dq_{rev}}{dT} \text{ ----------} \quad (30)$$

$\bar{C}$ = molar heat capacity.

The specific heat can be defined at constant pressure or at constant volume.

$$c_v = \frac{dq_v}{dT} = \left(\frac{\partial U}{\partial T}\right)_v \text{ ----------} \quad (31)$$

This is isochoric heat capacity (*dV= 0*)

$$c_p = \frac{dq_p}{dT} = \left(\frac{dU+PdV}{dT}\right) = \left(\frac{\partial H}{\partial T}\right)_p \text{ ----------(32)}$$

This is isobaric heat capacity

For ideal gas: $\bar{U} = \bar{U}(T)$ and $P\bar{V} = RT$

Hence, $\bar{H}(T) = \bar{U}(T) + RT$ ---------- (33)

Therefore,

$$\bar{c}_p = \frac{d\bar{H}}{dT} = \frac{d\bar{U}}{dT} + R = \bar{c}_v + R \text{ ---------- (34)}$$

The second Law of Thermodynamics and Entropy

There exist many statements of the 2nd Law of thermodynamics; all of them essentially, are equivalent. For example, Lord Kelvin postulated that: "No process is possible whose sole result is the conversion of heat to an equivalent amount of useful work"

Work can of course always be converted to heat, for example in the form of frictional losses, but Kelvin's statement tells us that it is impossible to retrieve this heat and convert it back entirely to work.

To understand the consequences of the 2nd Law, we shall investigate a cyclic process known as the Carnot cycle.

A Carnot cycle consists of four reversible steps: two isothermal and two adiabatic strokes carried out by a simple heat engine. (See figure 5)

It requires therefore 2 heat reservoirs (thermostats of "infinite" heat capacity) of temperatures T_1 and T_2 with $T_1 > T_2$ and a cylinder containing the working substance which will be assumed to be 'n' moles of a perfect gas.

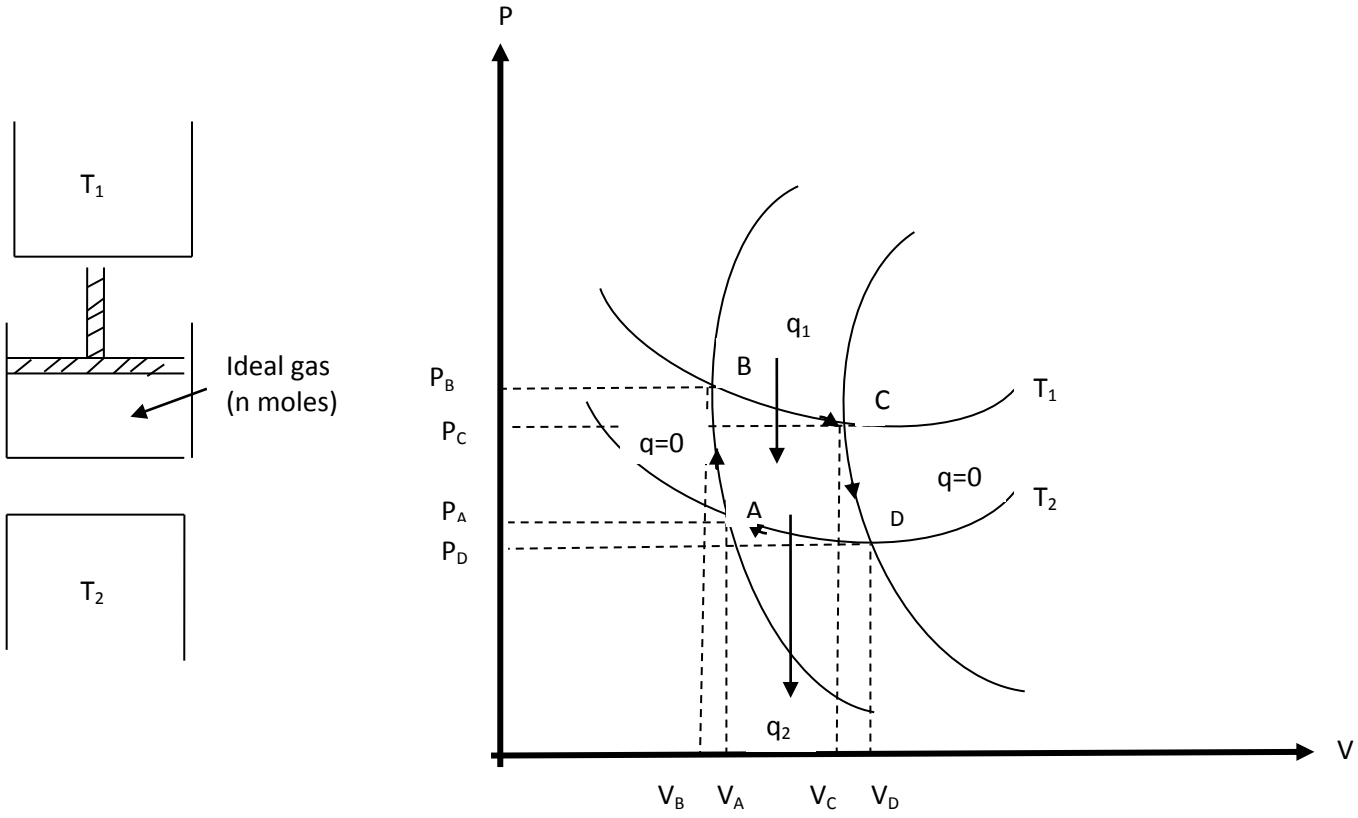


Figure 5

The process can be represented in a PV-diagram as shown figure 5.

Suppose the cycle starts at point A (Temperature T_2) where the cylinder is not connected to either T_1 or T_2. The gas is then slowly and adiabatically compressed until its temperature reaches T_1, at which point it is brought in thermal contact with reservoir T_1. Then follows a reversible isothermal expansion along BC, during which heat q_1 is absorbed from the reservoir and, an adiabatic expansion along CD. At that point, contact is made with reservoir T_2 and during the subsequent isothermal compression back to point A, heat $-q_2$ is lost by the gas and absorbed by the reservoir.

Now, according to the 1st Law, the amount of PV- work W, performed by the gas on the surrounding must be equal to:

$$q_1 + q_2 \quad \text{----------(35)}$$

Recall that along the isotherm the internal energy of a perfect gas is constant so that any heat absorbed (evolved) should exactly match the PV work done (absorbed).

Thus: $q_1 = \int_B^C PdV = nRT_1 \int_B^C \frac{dV}{V}$

$= nRT_1 ln\,(\frac{V_C}{V_B})$ ---------- (36)

And similarly.

$q_2 = -\,nRT_2 ln\,(\frac{V_D}{V_A})$ ---------- (37)

Let us now consider an infinitesimal $(dq = 0)$ adiabatic compression or expansion of the gas:

Since $dq = 0$ ---------- (38)

$du = -P\,dv$ (see 18) ----------(39)

At the same time, this change brings about a change in temp, *dT* such that:

$dU = c_v\,dT$ (see 31) ---------- (40)

At each point in the PV- diagram,

$PV = nRT$ ---------- (41)

So that small simultaneous change in P, V, and T will be given by

$Pdv + Vdp = nRdT$ ---------- (42)

Substituting $dT = \frac{dU}{c_v} = -P\,\frac{dV}{c_v}$ ---------- (43)

Gives:

$PdV + VdP = -\frac{nR}{C_V} PdV$ ---------- (44)

Or equivalently:

VdP = $-\left[1 + \frac{nR}{c_v}\right] PdV$ $= [-\frac{c_v+nR}{c_v} PdV]$ ---------- (45)

$Vdp = -\frac{c_p}{c_v} Pdv = -\gamma Pdv$ (see 34) ---------- (45b)

Where $\gamma = \frac{c_p}{c_v}$ ----------(46)

From (45)

$\frac{dP}{P} = -\gamma \frac{dV}{V}$ ---------- (47)

$d[lnP] = d\,[lnV]^{-\gamma}$ ----------(48)

Or $d[ln\,(PV^{\gamma})] = 0$ ----------(49)

Thus, along a reversible adiabatic:

$PV^{\gamma} = constant$ ---------- (50)

Since γ is obviously > 1, adiabatics are always "steeper" then isotherms, for which PV = constant.

Now for an adiabatic perfect gas, we can write:

$P_A V_A{}^{\gamma} = P_B V_B{}^{\gamma}$ ---------- (51)

and $P_D V_D{}^{\gamma} = P_C V_C{}^{\gamma}$ ---------- (52)

By dividing (51) by (52), we obtain

$\frac{P_A}{P_D}\left(\frac{V_A}{V_D}\right)^{\gamma} = \frac{P_B}{P_C}\left(\frac{V_B}{V_C}\right)^{\gamma}$ ---------- (53)

Note that A and D lie on the same isotherm and so do B and C, so that

$\frac{P_A}{P_D} = \frac{V_D}{V_A}$ ---------- (54)

and $\frac{P_B}{P_C} = \frac{V_C}{V_B}$ ---------- (55)

Hence $\left(\frac{V_A}{V_D}\right)^{\gamma-1} = \left(\frac{V_B}{V_C}\right)^{\gamma-1}$ ---------- (56)

or $\frac{V_D}{V_A} = \frac{V_C}{V_B}$ ----------(57)

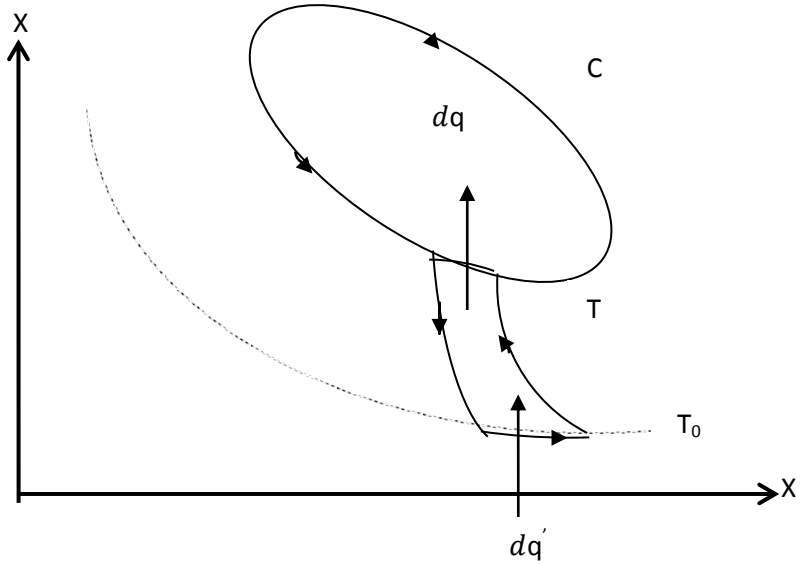
Now, from eqn (36) and (37), we see that

$\frac{q_1}{T_1} = \frac{q_2}{T_2}$ (For perfect gas) ---------- (58)

This is known as the Carnot – Clausius theorem.

Now let us consider a body (that is not real gas) undergoing an arbitrary cyclic process which is not necessarily reversible. The body is a closed system that may possess any degree of complexity. Imagine that the heat absorbed or ejected during the various stages of the cycle is supplied or drained off by an auxiliary cannot engine containing an ideal gas as the working substance.

The engine operates reversibly between the body and a large heat reservoir at temperature T_o and carries out a very large number of infinitesimal Carnot cycles until the main cycle C, is completed



For each such cycle,

$dq' = T_0 \frac{dq}{T}$……(59)

T is the momentary local temperature at which heat dq is absorbed by the body. Upon completion of the main cycle C, the total amount of heat dispensed by the reservoir is?

$\oint dq' = T_0 \oint \frac{dq}{T}$……(60)

According to the 1st law, since both the body and the Carnot engine would have returned to their respective original stokes after completion of the cycle C, the net amount of work performed in the main cycle and the Carnot cycles together should be equal to:

W= $\oint dq + \oint (dq' - dq) = \oint dq'$…….. (61)

ie, W equals the net amount of heat absorbed from the reservoir. But then, the 2nd law demands that $\oint dq'$ cannot be +ve, and hence, $\oint dq/T \leq 0$…….(62) for any cyclic process.

In particular, if C is a reversible cycle, driving the process backwards would lead to the additional requirement:

$\oint dq/T \geq 0$…….(63)

Both conditions can only be met simultaneously if: $\oint dq_{rev} = 0$…….. (64) for any reversible cycle.

The above property is the hallmark of a function of state with exact differential

$$dS = \frac{dq_{rev}}{T}$$……(65)

This new form of state, S, is called the entropy of the system. It is an extensive quantity, expressed in J/K. The difference in the entropy of a system between two states A and B is:

$S_B - S_A = \int_A^B ds = \int_A^B \frac{dq_{rev}}{T}$…….. (66)

For a reversible change in a closed system: the 1st law can be reformulated to be:

$dU = TdS + dW_{rev}$…… (67)

$\Rightarrow dU = TdS - PdV$……(68)

Also, we can now write c_v and c_p in terms of the entropy:

$c_v = T\,(dS/dT)v$
$c_p = T\,(dS/dT)p$ ---------- (69)

From equation (69), two expansion coefficients may be defined thus:

The coefficient of thermal expansion: β

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \ldots\ldots\ldots\ldots\ldots\ldots\ldots (69a)$$

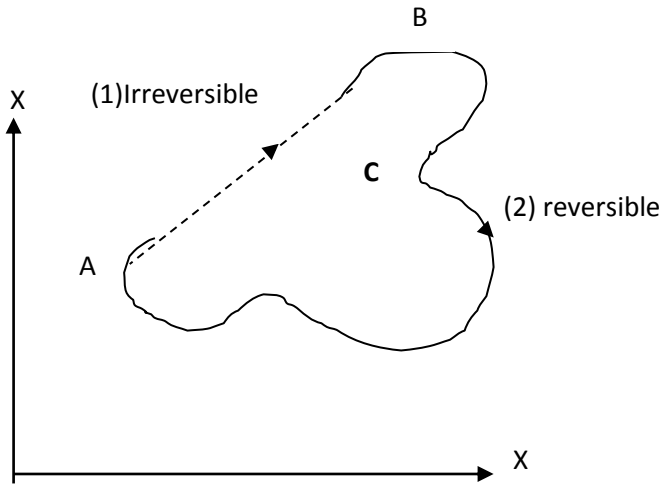
The coefficient of isothermal compressibility, K

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \ldots\ldots\ldots\ldots\ldots\ldots\ldots (69b)$$

For an irreversible cycle, we see that

$\oint dq/T < 0$……..(70)

Consider a system comprising of an irreversible (A-B) reversible (B-A) processes



$\oint dq/T = \int_A^B \frac{dq_{irrev}}{T} + \int_B^A \frac{dq_{rev}}{T} < 0$ …….. (71)

Which is equivalent to:

$S_B - S_A = \int_A^B \frac{dq_{rev}}{T} > \int_A^B \frac{dq_{irrev}}{T}$……..... (71b)

In general,

$dS \geq \frac{dq}{T}$ …… (72)

In particular, for an adiabatic change ($dq = 0$)

$dS \geq 0$ ……(73)

A change in the total entropy $S_t = S + S_{surr}$ then always has to obey the inequality

$(\Delta S_t)_{u,v} \geq 0$ ……..(73b)

The 2nd law may now be stated as follows: During a spontaneous process, the total entropy of an isolated system increases. It remains constant for reversible changes of state. At this point, it may be instructive to mention an alternative approach to the concept of entropy, which uses the fact that matter is actually composed of atoms and molecules. This formulation is due to L. Boltzmann:

$$S = KlnW \quad \ldots\ldots\ldots\

$$H = U + PV \quad \text{..... (4)}$$

We are more interested in the change of enthalpy dH, which is a measure of the heat of reaction when a system changes state.

$$dH = dU + PdV + VdP \quad \text{..... (5)}$$

Helmholtz free Energy, F

This is the minimum amount of work obtainable in which there is no change in temperature. It is a function and is defined as:

$$F = U - TS \quad \text{..... (6)}$$

The change in Helmholtz free energy is given by

$$dF = dU - TdS - SdT$$
$$= -PdV - SdT \quad \text{..... (7)}$$

Gibbs Free Energy, G

This is the maximum amount of work obtainable in which there is no change in volume It is a state function and is defined as:

$$G = H - Ts \quad \text{..... (8)}$$

$$dG = dH - Tds - SdT = VdP - SdT \quad \text{(see equations 5 and 3)}$$

It is obvious that

$$\Delta G = \Delta F + \Delta(PV) \quad \text{..... (9)}$$

Chemical Potential

This is important when the quantity of matter is not fixed (e.g we are dealing with a changing number of atoms within a system). When this happens, we have to modify our thermodynamic relations to take account of this.

$$dU = TdS - PdV + \mu dN$$
$$dF = -PdV - SdT + \mu dN \quad \text{..... (10)}$$
$$dG = VdP - SdT + \mu dN$$

This means that there are several ways of writing the chemical potential μ

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \left(\frac{\partial G}{\partial N}\right)_{T,P} \quad \ldots\ldots\ldots\

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \; and \; \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \; (19)$$

(using equation 14 and 15 respectively)

Also from *dH,*

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\

also generate entropy. This is still not enough to ensure phase equilibrium. This is a dynamic equilibrium for which rate of evaporation from L = rate of condensation from V.

Now consider a reversible process in which one mole of liquid is transferred to the vapor phase by slowly raising the piston while simultaneously absorbing heat q_{rev}. from the reservoir. For this closed system the energy balance can be put in the form:

$$\Delta\bar{U} + T\Delta\bar{S} - P\Delta\bar{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where

$$\left.\begin{array}{l} \Delta\bar{U} = \overline{U_V} - \overline{U_L} \\ \Delta\bar{S} = \bar{S}_V - \bar{S}_L \\ \Delta\bar{V} = \bar{V}_V - \bar{V}_L \end{array}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Eqn. (1) may also be written as:

$$\left(\Delta\overline{H}_{vap}\right)_P = T\Delta\bar{S}(= q_{rev}) \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Eqn. (3) defines the latent heat or molar enthalpy of vaporization

Hence, substitution for eqn. (2) and rearranging, gives the required condition, known as material equilibrium:

$$\bar{U}_V + P\bar{V}_V - T\bar{S}_V = \bar{U}_L + P\bar{V}_L - T\bar{S}_L \ldots\ldots\ldots\ldots (4)$$

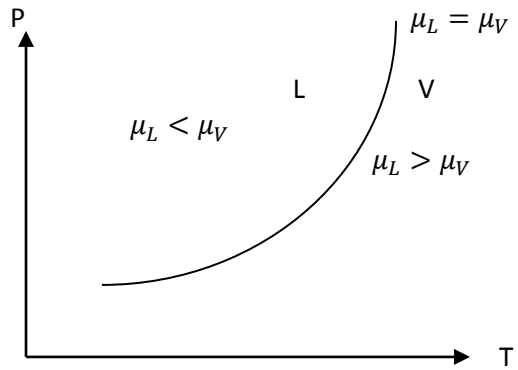
Or

$$\bar{G}_V(T,P) = \bar{G}_L(T,P) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\mu_V(T,P) = \mu_L(T,P) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

This is an equation in terms of T and P, which could be solved, in principle, to give P as a function of T, where P is the saturation pressure.

In a P –T or phase diagram, this relationship defines a co- existence line for L/V equilibrium



An alternative approach to the problem of material equilibrium is based on the fact that the G of a closed system is at a minimum if P and T are held fixed: $(\partial G)_{T,P} = 0$; and may serve to illustrate the use of this minimum principle. G can be written alternatively as

$$G = G_L + G_V = n_L\mu_L + n_V\mu_V \ldots\ldots\ldots (7)$$

Where G is extensive

$n = n_L + n_V = constant$ …….. (8)

Noting that μ_L and μ_V are both constant during this change and $\partial n_L = -\partial n_V$

$\therefore (\partial G)_{T.P} = (\mu_V - \mu_L)\partial n_V$ ……. (9)

And for this to be zero, we need $\mu_L = \mu_V$

For non- equilibrium states i.e. when T and P are uniform but $\mu_L \neq \mu_V$

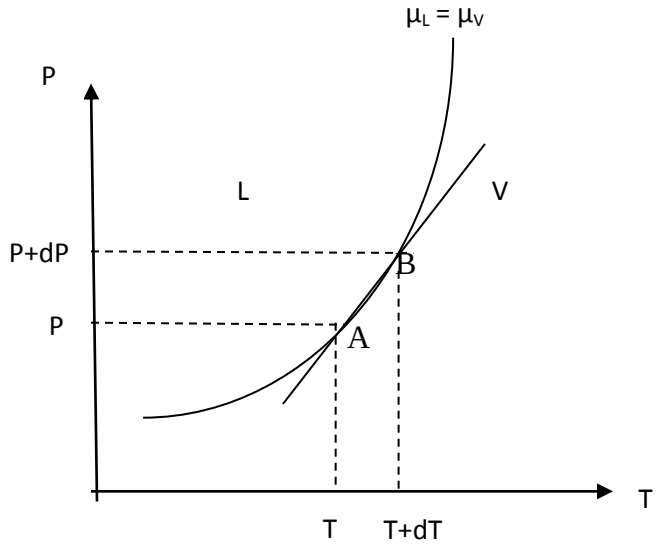
If $\mu_L > \mu_V$, then

$(\partial G)_{T.P} = (\mu_V - \mu_L)\partial n_V < 0$ if $dn_V > 0$ i.e. G decreases if liquid evaporates.

This situation arises for (T,P) combinations below the saturation curve in the diagram; here V is more stable than L. Conversely, above this curve, $\mu_L < \mu_V$ and so L is the more stable phase. Thus, the P_{Sat} (T) curve divides P – T plane into stability regions.

This example is illustrative of a more general principle which states that whenever μ is not uniform, matter will flow spontaneously from places with the higher to places with the lower μ (hence the name: chemical potential).

Now, let us return to the coexistence curve and see what general conclusions may be drawn regarding its functional form. Suppose that the system moves from point A with coordinates T and P to a nearby point B, also on the curve, at T + d T, P +d P.



Since equilibrium is maintained, it is true that $d\mu_L = d\mu_V$ for this change of state. Now given that, $\mu_{L,V} = \frac{G_{L,V}}{n_{L,V}}$

$d\mu_{L,V} = -\bar{S}_{L,V}\, dT + \bar{V}_{L,V}\, dP$ ..... (10)

Hence, $-\bar{S}_L\, dT + \bar{V}_L\, dP = -\bar{S}_V\, dT + \bar{V}_V\, dP$ ..... (11

Therefore, $\left(\frac{dP}{dT}\right)_{sat} = \frac{\bar{S}_V - \bar{S}_L}{\bar{V}_V - \bar{V}_L} = \frac{\Delta\bar{S}}{\Delta\bar{V}}$ ... ... (12)

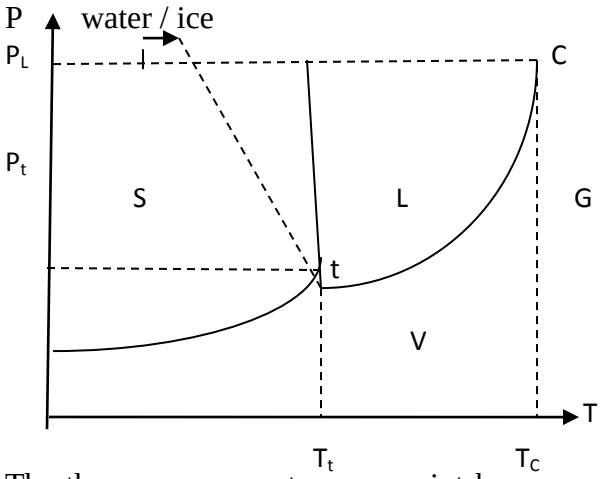
Which can also be written as:

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{\Delta\overline{H}_{vap}}{T\,\Delta\bar{V}} \text{ ... ... (13)}$$

This is the Clausius - Clapeyron equation which relates the slope of the tangent to the P_{sat} Vs T curve at each point to the volume and latent heat of vaporization at the same point. It applies generally to the so –called 1st order phase transition, i.e. those wih $\Delta\bar{s} \neq 0$ and $\Delta\bar{V} \neq 0$, which is the case for most phase equilibrium of chemical interest.

What has been said about L/V equilibrium applies equally to solid / liquid (S/L) and solid / vapour (S /V) equilibria. For each case, a Clausius- Clapeyron equation can be formulated with $\Delta\overline{H}_{vap}$ replaced by the latent heat of fusion ($\Delta\overline{H}_{fus}$) and sublimation ($\Delta\overline{H}_{sub}$) respectively, and

similarly for the molar volumes of transformation. These equilibria are also represented by coexistence lines in a P –T diagram.



The three curves meet at one point known as the triple point, t (T_t , P_t), where all three phases coexist. Two equilibrium conditions:

$$\mu_L(T_t, P_t) = \mu_V\,(T_t, P_t) = \mu_S\,(T_t, P_t) \ldots\ldots\ldots (14)$$

should be obeyed simultaneously at this point, which determine its position unambiguously (for water, $T_t \simeq 298k, P_t$ =6 x 10^{-3} atm.).

Another important feature of a P – T diagram is the critical point (C), which marks the temperature T_C above which vapour can no longer be condensed, no matter how high the applied pressure. Only a homogeneous gas phase (G) can exist for $T > T_C$.

For most substances, the coexistence lines have positive slopes. A notable exception is water, where the melting line has a negative slope because $\Delta\bar{V}_{fus} < 0$ (ice has a lower density than water, that is why it floats), so that increasing the pressure on ice at constant T will eventually cause it to melt.

Now if the vapour is assumed to behave approximately as a deal gas, then

$$\bar{V}_V \approx RT/P_{sat} \ldots\ldots\ldots (15)$$

This implies that $\overline{V_V} \gg \bar{V}_L, \bar{V}_S$ hence $\Delta\bar{V} \approx \bar{V}_V$ …… (16)

Subs. (15) and (16) into Clausiuns –Clapeyron equation gives:

$$\frac{dP_{sat}}{dT} = \frac{P_{sat}\Delta\overline{H}}{RT^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Rearranging:

$$\frac{dP_{sat}}{P_{sat}} = \frac{\Delta\overline{H}}{R}\ \frac{dT}{T^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (18$$

Which is equivalent to:

$$\frac{dlnP_{sat}}{d\left(\frac{1}{T}\right)} = -\frac{\Delta\overline{H}}{R} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

If $\Delta\overline{H}_{vap}$ or $\Delta\overline{H}_{sub}$ can be regarded as constant (this is a good approximation with a broad range of temperatures), this result implies that a plot of $lnP_{sat}\ Vs\ \frac{1}{T}$ should produce a straight line with negative slope $-\frac{\Delta\overline{H}}{R}$.

If $\Delta\overline{H}_{vap}, \Delta\overline{H}_{sub}, and\ \Delta\overline{H}_{fus}$ are constant, knowledge of any two of them allows the third to be calculated based on the argument that, at the triple point, sublimation of 1 mole of solid can either take place directly or proceed in two steps ,namely: as melting followed by evaporation: 1 mol S → 1 mol L → 1 mol V. The net $\Delta\overline{H}$ is the same in each case (Hess'law), therefore:

$$\Delta\overline{H}_{sub} = \Delta\overline{H}_{fus} + \Delta\overline{H}_{vap}$$

It Should be pointed out that the phase diagram by itself does not contain sufficient information to help us understand the process of phase transformation. It often happens that a phase transition does not occur when one would expect it based on the phase diagram. A liquid may persist in a metastable super heated or super cooled state, or a vapour may be cooled below the boiling point without condensation (supersaturated vapour). These phenomena occur because a new phase never appeared in bulk form all at once, but rather changes from the "parent" phase in the form

of small bubbles, crystals or droplets which initially have a high, energetically unfavorable, area-to- volume ratio.

The result is that a relatively high surface (free) energy creates a nucleation barrier against the onset of phase transformation. This barrier may be overcome by agitation or by "seeding" I.e. providing a rough surface to kick – start the nucleation of the new phase (for instance: this is the reason for adding solid chips to a liquid prior boiling, so as to prevent overheating and "bumping") Otherwise, nucleation is a purely random (stochastic process).

Kinetic Theory of Gases

The Kinetic theory of gases attempts to explain all of the concepts of classical thermodynamics, such as temperature and pressure, in terms of an underlying microscopic theory based on atoms and molecules. One of the most fundamental properties of any macroscopic system is the so-called equation of state. This is the equation that specifies the exact relation between pressures P, volume V, and temperature T for a substance. The equation of state for a gas is very different to the equation of state of a liquid. Now, it turns out that most gases obey a simple equation of state called the ideal law

$$PV = n RT$$

We may also write the equation of state in the form:

$$f (P, V ,T) = 0$$

where the function f depends on the particular system. The simplest system is an ideal gas. In this case, the equation of state is:

$$PV = N K T$$

where N = Number of particles, and K is the Boltzmann constant. For Vander Waal's gas, the equation of state is:

$$\left(\mathrm{P} + \frac{a}{V^2}\right)(\bar{V} - b) = RT$$

Where a and b are constants

Note that:

$R = N_A K$

$\bar{V} = \frac{V}{n}$

$n = \frac{N}{N_A}$

Where n is number of moles

N = number of molecules

NA = Avogadro's number = 6.02×10^{23} Mole $^{-1}$

$$\therefore \ \mathrm{N} = \mathrm{n}\,\mathrm{N_A}$$

The equation of state of a Vander Waal's gas reduces to that of an ideal gas for a = b = 0.

The equation of state can be represented on a graph of pressure Vs. Volume, often called a PV diagram.

Example1: Derive a formular for the work done by any gas (ideal or not) which expands isobarically

Solution: If *P* is a constant then,

$$W = \int_{V_i}^{V_f} P dV = P \int_{V_i}^{V_f} dV$$
$$= P[V]_{V_i}^{V_f}$$
$$= P(V_f - V_i)$$
$$= P\Delta V$$

Example2: Derive a formular for the work done by a gas when it expands isothermally.

Solution: The work done by an expanding gas is given by:

$$W = \int_{V_i}^{V_f} P dV$$

Where V_f is the final volume, V_i is the initial volume, P is the pressure

But this pressure changes. For an ideal gas we have:

$$P = \frac{nRT}{V}$$

$$\Rightarrow w = nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

$$= nRT[lnV]_{V_i}^{V_f} = nRT(lnV_f - lnV_i)$$

$$= nRTln\left(\frac{V_f}{V_i}\right)$$

THE MAXWELL DISTRIBUTION

The Maxwell distribution of velocities describes the thermal motions of distribution of classical particles.

Consider a one-dimensional (along *x*-axis say) system of ideal particles of mass *m*. The distribution function $f(x, v_x, t)$, is such that $f(x, v_x, t)\, dxdv_x$ is the probability of finding a particle between *x* and *x+dx* with velocity between v_x and $v_x + dv_x$. The total probability must be equal to unity so we have:

$$\int_{-Lx/2}^{Lx/2} \int_{-\infty}^{\infty} dv_x f(x, v_x, t) = 1 \ \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where L_x is the length of the system.

The Maxwell distribution applies to a thermal distribution, at a temperature T. It is stationary (independent of *t*) and homogeneous (independent of *x*) with the specific form as:

$$F(v_x) = \frac{1}{L_x}\left(\frac{m}{2\pi KT}\right)^{1/2} exp\left[\frac{-mv_x{}^2}{2KT}\right] \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Now, the standard integral:

$$\int_{-\infty}^{\infty} dx\, e^{-x^2/2} = (2\pi)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

For a particle in *3 - D*, equation (1) becomes

$$\int d^3\mathrm{x}\, d^3v f(x, v, t) = 1 \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

with,

$d^3\mathrm{x}d^3v = dx\ dy\ dz\ dv_x\ dv_y\ dv_z$ in Cartesian coordinate

$= r^2 dr d\cos\theta\ d\emptyset v^2 dv d\cos\theta_v\ d\emptyset_v$ in spherical polar coordinates ……. (5)

Similarly in *3 – D*, equation (2) becomes,

$$f(v) = \frac{1}{V}\left(\frac{m}{2\pi KT}\right)^{3/2} exp\left[\frac{-mv^2}{2KT}\right] \text{……. (6)}$$

Where V is the volume of the system

A Maxwellian distribution corresponds to a distribution of the form: $\varepsilon exp[-\varepsilon/KT]$ where $\varepsilon = \frac{1}{2}mv^2$ is the K.E of the particle. This form generalizes a canonical distribution for the state with energy ε of any system.

We are only concerned (at the present) with the case of a classical ideal gas.

Thermodynamics of an Ideal Gas

The basic properties of an ideal gas can be calculated using the Maxwellian distribution function. Two important quantities are the internal energy and the pressure for a given N, V & T.

The internal energy of an ideal gas consisting of N particle in a volume V at a temperature T may be evaluated as follows: The energy of each individual particle is $\varepsilon = \frac{1}{2}mv^2$, and the total energy is found by summing oven all the particles in the system. The total energy for a statistical distribution is N times the mean energy where,

Mean energy = $<\varepsilon> \int d^3\,\mathrm{x}\, d^3v\ \varepsilon f(v)$ ……. (7)

i.e., $U = N < \varepsilon >$.

⇒ Evaluating the mean energy of the particles by averaging over the Maxwellian distribution (equation 6) gives

$$U = \frac{3}{2}NKT \text{ ……. (8)}$$

Which is the internal energy of an ideal gas. If the gas consists of particles (such as molecules) that can rotate or oscillate, then Equation (8) generalizes to $U = \frac{g}{2}NKT$ where g is the number of degrees of freedom. The specific form of equation (8) corresponds to $g = 3$ degrees of freedom for a structure-less particle with these being its motion in the x, y, z directions for example.

The Equation of State of an Idea Gas

Another property of an ideal gas is the equation of state. The pressure may be calculated by noting that it is the force per unit area on the surface of the system.

Consider a system which is a cube of sides L, so that its volume is $V = L^3$. Consider the force on the surface in the $y - z$ plane. Each particle that reflects from the surface has v_x change sign. This corresponds to am impulse, $2mv_x$. The problem reduces to a one-dimensional problem because the v_y and v_z components are unaffected.

The number of particles between v_x and $v_x + dv_x$ reflecting from the plane per unit time is $v_x f(v_x) dv_x / L$. The force exerted is ∴

$$\frac{1}{L}\int_{\infty}^{\infty} dv_x \, 2m{v_x}^2 f(v_x) \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Evaluating this for a Maxwellian distribution, and dividing by the area L^2 to get the force per unit area gives.

$$P = \frac{1}{L^3}\int_{-\infty}^{\infty} dv_x \, 2m{v_x}^2 f(v_x) = \frac{NKT}{V} \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Equation (10) is the perfect gas Law.

The Entropy of an Ideal Gas

The entropy determines whether or not a change can occur spontaneously: a change can occur only if the entropy does not increase. The thermodynamics of an ideal gas can be

determined given the equation of state. $PV = NKT$, and the assumption that C_v is independent of temperature. In particular, one may then derive explicit expressions for the entropy and for all the state functions.

from $dU = TdS - PdV$, with $U = C_vT$ and $PV = NKT$, we have

$$dS = C_v\frac{dT}{T} + NK\frac{dV}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

$$\Rightarrow \int dS = \int C_v\frac{dT}{T} + \int NK\frac{dV}{V} \quad \ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$\Rightarrow\ S = S_0 + C_v ln\left(\frac{T}{T_0}\right) + NKln\left(\frac{V}{V_0}\right) \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Where S_0, T_0 and V_0 are constants of integration.

Now, for a monatomic gas, $C_v = \frac{3}{2}NK$,

$$\therefore\ \ S = S_0 + NKln\left(\frac{T^{3/2}V}{{T_0}^{3/2}V_0}\right) \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Combining all the constants in (13) and (14) into a single constant, and with $C_v/NK = {}^3/_2$ the entropy can then be written as:

$$S = constant + NKln(T^{C_v/NK}V) \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

The Adiabatic Equation of State

Consider changes at constant entropy, called adiabatic changes. An adiabatic change is reversible.

For an ideal gas, $dS = 0$ in (11) implies that $C_v\frac{dT}{T} + NK\frac{dV}{V} = 0$ $\ldots\ldots\ldots\ldots\ldots\ldots (16)$

Integrating (16), we find that $ln(T^{C_v}.V^{NK}) = constant$ $\ldots\ldots\ldots\ldots\ldots\ldots (17)$

Eliminating T using PV= NKT, this relation may be rewritten in the form

$$PV^{\Gamma} = constant, \Gamma = \frac{C_v + NK}{C_v} \quad \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Where Γ is called the adiabatic index.

For a monatomic gas, one has $C_v = {}^3/_2\, NK$ and hence $\Gamma = {}^5/_3$

The Entropy of Mixing

A simple example of the increase in entropy is when two gases mix. Consider a system at a fixed temperature, in which initially there are N_1 particle in a volume V_1 and N_2 particles in a volume V_2, and that these are allowed to mix so that there $N_1 + N_2$ particles in a volume $V_1 + V_2$. The change in entropy is:

$$\Delta S = (N_1 + N_2)Kln(V_1 + V_2) - N_1 K ln V_1 - N_2 K ln V_2$$

$$= Kln\left(\frac{(V_1 + V_2)^{N_1+N_2}}{{V_1}^{N_1}{V_2}^{N_2}}\right) \ldots\ldots\ldots\ldots\ldots\ldots (19)$$

In the particular case when $V_1 = V_2 = {}^V/_2$, $N_1 = N_2 = {}^N/_2$, equation (19) reduces to:

$$\Delta S = NKln2 \ \ldots\ldots\ldots\ldots\ldots\ldots (20)$$

It follows that the entropy increases in this case and it is not difficult to see that the entropy change as a result of mixing is always positive.

Remark: we have not said whether the gases are identical or not. If they are identical then the change in entropy must be zero, and yet the calculation seems to suggest that there is a change in entropy. This is referred to as the Gibb's Paradox. There is no simple physical resolution of the Gibbs Paradox within the framework of classical statistical mechanics.

There is a procedure, called correct Boltzmann counting, which makes classical statistical mechanics internally consistent. However, a proper justification of correct Boltzmann counting relies on the classical limit of quantum statistical mechanics.

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