HEAT AND THERMODYNAMICS

UNIT – II
US05CPHY23

By
Dr. Jagendra K. Baria
Professor Of Physics
V. P. & R. P. T. P. Science College
Vidyanagar 388 120

Prof. J. K. Baria

2.1. T-S Diagram for a Pure Substance

The entropy of a system is a function of the thermodynamic coordinates whose change during a process in which the system goes from an equilibrium state *i* to another equilibrium state *f* is equal to

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

Where the symbol R indicates that the integration is to be performed over any reversible path connecting *i* and *f*.

If the two equilibrium states are infinitesimally close, then,

$$dQ = T\,dS \text{ and } \frac{dQ}{dT} = T\,\frac{dS}{dT}$$

At constant volume, $$\left(\frac{dQ}{dT}\right)_V = C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

And at constant pressure, $$\left(\frac{dQ}{dT}\right)_P = C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

2.1. T-S Diagram for a Pure Substance

If the temperature variation of C_V is known, the entropy change during an isochoric process may be calculated from the equation

$$S_f - S_i(isochoric) = \int_i^f \frac{C_V}{T}\, dT$$

Similarly, for an isobaric process,

$$S_f - S_i(isobaric) = \int_i^f \frac{C_P}{T}\, dT$$

The above equations provided a general method for calculating an entropy change but no way of calculating the absolute entropy of a system in a given state. If a set of tables is required that is to be used to obtain entropy differences and not absolute entropy, then it is a convenient to choose an arbitrary standard state and calculate the entropy change of the system from this standard state to all other states. Thus, in the case to all other states. Thus, in the case of water, the standard state is chosen to be that of saturated water at 0.01^0C and its own vapor pressure 4.58 mm, and all entropies are referred to this state.

2.1. T-S Diagram for a Pure Substance

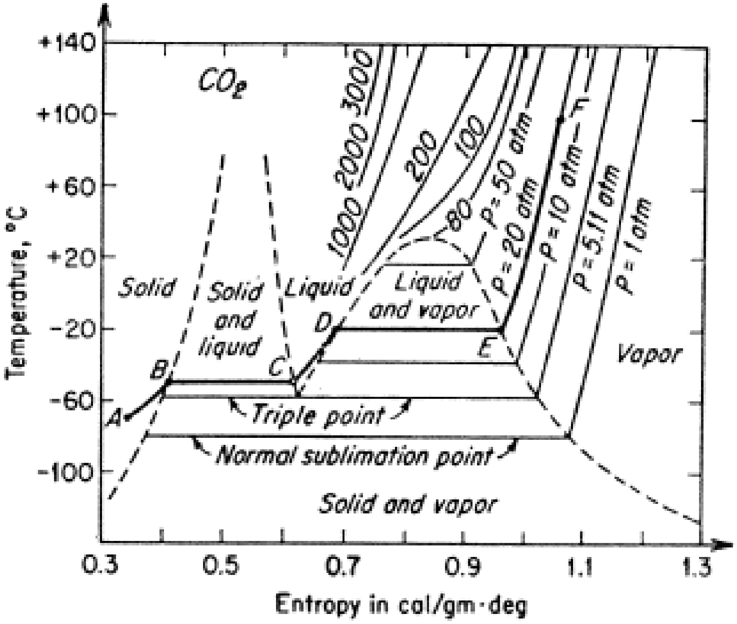


Fig. 2.1. T-S diagram for CO_2. The two dashed lines bounding the solid-liquid region are a guess.

The T-S diagram for a substance such as CO_2 is shown in fig. 2.1 the curve from A to F is a typical isobar representing a series of reversible isobaric processes in which solid is transformed finally into vapor. Thus,

AB = isobaric heating of solid to its melting point

BC = isobaric isothermal melting

CD = isobaric heating of liquid to its boiling point

DE = isobaric isothermal vaporization

EF = isobaric heating of vapor (superheating)

The area under the line BC represents the heat of fusion at the particular temperature, and the area under the line DE represents the heat of vaporization. Similarly, the heat of sublimation is represented by the area under any sublimation line. It is obvious from the diagram that the heat of vaporization decreases as the temperature rises and becomes zero at the critical point and also that the heat of sublimation is equal to the sum of the heat of fusion and the heat of vaporization at the triple point.

2.2. Gibbs U-V-S Surface

For an infinitesimal process, we have, $dU = dQ - P\,dV$

If the process takes place between two neighboring equilibrium states, we may assume it to be reversible, Hence, $dU = T\,dS - P\,dV$ ... (1)

Regarding U as a function of S and V, we may write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \qquad ....(2)$$

Comparing equation (1) and (2) we have

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \ \left(\frac{\partial U}{\partial V}\right)_S = -P$$

It is clear from the above that a surface, generated by plotting U, S and V, would also indicate the temperature and pressure from the two slopes at any given point. Gibbs was the first to consider such a surface and to point out its interesting properties. A rough diagram of a U-V-S surface for water is given in fig. 2.2.

2.2. Gibbs U-V-S Surface

Imagine a plane at S = S_0 cutting the surface, the intersection being a particular curve whose equation involves U and V. The slope of this curve at some point on the curve, say (U_0, V_0, S_0) is $(\partial U/\partial V)_0$, and the equation of the line tangent to the curve at this point is $U - U_0 - \left(\frac{\partial U}{\partial V}\right)_0 (V - V_0) = 0$

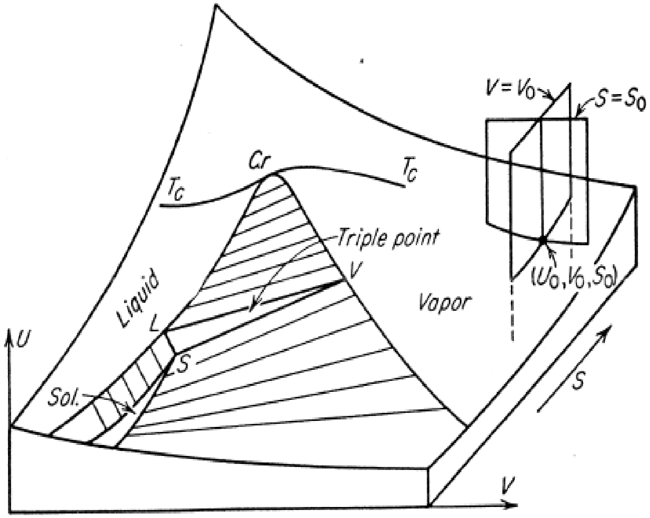


Fig. 2.2 Gibbs U-V-S surface for water.

Again upon cutting the surface with a plane at V = V_0, curve is obtained the equation of whose tangent line at the point (U_0, V_0, S_0) is

$$U - U_0 - \left(\frac{\partial U}{\partial S}\right)_0 (S - S_0) = 0$$

Now the plane that is tangent to the surface at the point (U_0, V_0, S_0) contains these two intersecting tangents lines. Therefore the equation of the plane tangent to the surface at the point (U_0, V_0, S_0) is

$$U - U_0 - \left(\frac{\partial U}{\partial V}\right)_0 (V - V_0) - \left(\frac{\partial U}{\partial V}\right)_0 (S - S_0) = 0$$

Prof. J. K. Baria

2.2. Gibbs U-V-S Surface

Calling P_0 and T_0 the pressure and temperature, respectively, at the point in question we have $\left(\frac{\partial U}{\partial V}\right)_0 = -P_0$ & $\left(\frac{\partial U}{\partial S}\right)_0 = T_0$

And the equation of the tangent plane becomes, $U - U_0 + P_0 (V - V_0) - T_0 (S - S_0) = 0$

Consequently, the P and T of a point determine uniquely a tangent plane at the point. If two different points on the surface therefore refer to the same pressure and temperature, they must both touch the same tangent plane.

Further, if P and T are constant along a curve, this whole curve touches the tangent plane and is therefore a straight line. An isothermal isobaric vaporization must therefore be a straight line. Since the whole liquid vapor region is constructed of such lines, it is a ruled surface. The same is also true of the other two mixture regions. Since all proportions of sold, liquid, and vapor exist at the same pressure and temperature, it is clear that the tangent plane determined by this P and T must touch all these points or in other words, the triple point on a U-V-S surface is a plane triangle. A tangent plane touches the surface in the solid region or the vapor region or the liquid region at only one point.

It should be emphasized that the surface depicted qualitatively in fig. 2.2 represents only equilibrium states of water. The original surface anticipated by Gibbs included metastable states such as those corresponding to supercooled vapor and supercooled liquid. *A model showing these metastable states was first made by Maxwell during Gibbs's lifetime and was presented to him.*

2.3. Enthalpy

The enthalpy of a system is defined as $H = U + P\,V$

In order to study the properties of this function, consider the change in enthalpy that takes place when a system undergoes an infinitesimal process from an initial equilibrium state to a final equilibrium state. We have $dH = dU + P\,dV + V\,dP$

But $dQ = dU + P\,V$ Therefore, $dH = dQ + V\,dP$

Dividing both sides by dT, $\frac{dH}{dT} = \frac{dQ}{dT} + V\,\frac{dP}{dT}$

and, at constant P, $\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{dQ}{dT}\right)_P = C_P$ $[property\ (1)]$

Since,

$dH = dQ + V\,dP,$

The change in enthalpy during an isobaric process is equal to the heat transferred. That is,

$$\left.\begin{array}{l} H_f - H_i = Q \\ \text{Or} \\ H_f - H_i = \int_i^f C_P\ dT \end{array}\right\}$$

(Isobaric) (*property (2)*]

2.3. Enthalpy

Since isobaric processes are much more important in engineering and chemistry than isochoric processes, the enthalpy is of greatest use in these branches of science.

The change in enthalpy of a system undergoing an adiabatic process has an interesting graphical interpretation. Since

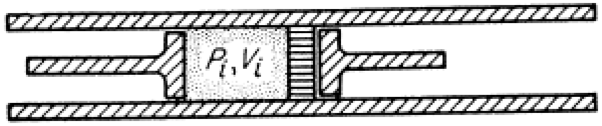
$dH = dQ + V\,dP,$

Then for an adiabatic process

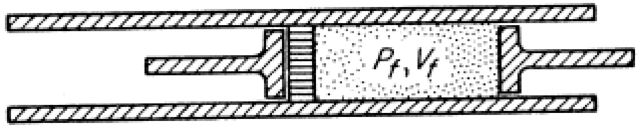
$H_f - H_i = \int_i^f V \; dP$ (adiabatic) [*Property (3)*]

The above integral represents the area to the left of an adiabatic curve on a P-V diagram. This area does not represent work.

2.3. Enthalpy



(i) Initial state



(f) Final state

Fig. 2.3. Throttling process.

One of the most interesting properties of the enthalpy function is in connection with a throttling process. Imagine a cylinder thermally insulated and equipped with two non-conducting pistons on opposite sides of a porous wall, as shown in fig 2.3(i). The wall shaded in horizontal lines, is a porous plug, a narrow constriction, or a series of small holes. Between the left hand piston and the wall there is a gas at a pressure P_i and a volume V_i; and since the right hand piston is against the wall, any gas being thus prevented from seeping through, the initial state of the gas is an equilibrium state. Now imagine moving both pistons simultaneously in such a way that a *constant pressure P_i is maintained on the left hand side of the wall and a constant lower pressure P_f is maintained on the right hand side.* After all the gas has seeped through the porous wall, the final equilibrium state of the system will be as shown in fig. 2.3(f). Such a process is a throttling process.

A throttling process is obviously an irreversible one since the gas passes through non-equilibrium states on its way from the initial equilibrium state to its final equilibrium state.

2.3. Enthalpy

non-equilibrium states cannot be described by thermodynamic coordinates, but an interesting conclusion can be drawn about the initial and final equilibrium states. Applying the first law to the throttling process

$$Q = U_f - U_i + W$$

We have $Q = 0$

And

$$W = \int_0^{V_f} p \; dV + \int_{V_i}^{0} P \; dV$$

Since both pressures remain constant

$$W = P_f V_f - P_i V_i$$

The above expression is known in engineering as flow work, since it represents the work necessary to keep the gas flowing. Therefore,

$0 - U_f - U_i + P_f V_f - P_i V_i$

Or $U_i + P_i V_i = U_f + P_f V_f$

and finally

$H_i = H_f$ (Throttling process) [*property (4)*]

In a throttling process therefore, the initial and final enthalpies are equal.

2.3. Enthalpy

One is not entitled to say that the enthalpy remains constant since one cannot speak of the enthalpy of a system that is passing through such nonequlibrium states.

In plotting a throttling process on any diagram the initial and final equilibrium states may be represented by points. The intermediate states, however, cannot be plotted.

A continuous throttling process may be achieved by a pump that maintain a constant high pressure on one side of a constriction or porous wall and a constant lower pressure on the other side as shown in fig. 2.4. For every unit of mass that undergoes the throttling process we may write.

$$h_i = h_f$$

Where the lower case letters indicate *specific enthalpy.*

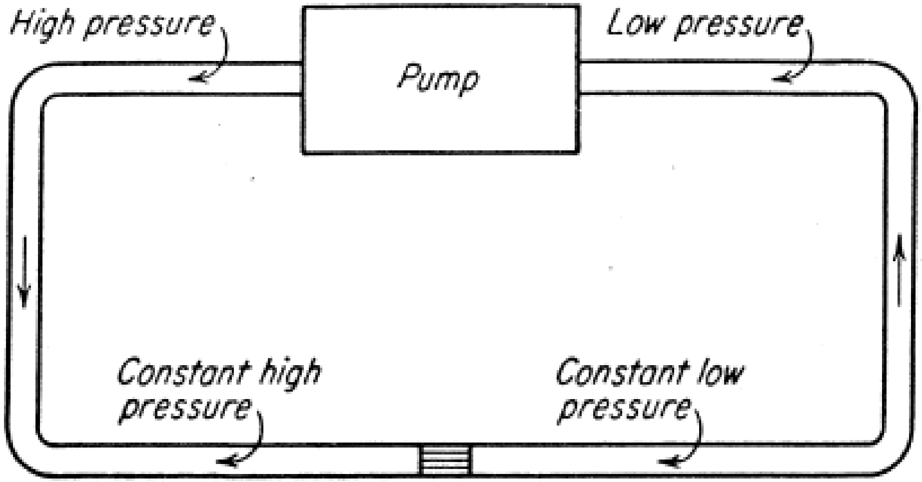


Fig. 2.4. Apparatus for performing continuous throttling process.

2.3. Enthalpy

Table 2.1 comparison of U and H

Internal energy U	Enthalpy H
In general $dU = dQ - PdV\ ,\ \left(\frac{\partial U}{\partial T}\right)_V = C_V$	In general $dH = dQ + V\,dP,\ \left(\frac{\partial H}{\partial T}\right)_P = C_P$
Isochoric Process $U_f - U_i = Q$ $U_f - U_i = \int_i^f C_v\ dT$	Isobaric Process $H_f - H_i = Q$ $H_f - H_i = \int_i^f C_P\ dT$
Adiabatic Process, $U_f - U_i = \int_i^f P\,dV$	Adiabatic Process , $H_f - H_i = \int_i^f V\,dP$
Free Expansion, $U_i = U_f$	Throttling process, $H_i = H_f$
For an ideal gas, $U = \int C_V\,dT + Const$	For an ideal gas, $H = \int C_P\,dT + Const$

Prof. J. K. Baria

2.4. Helmholtz Function.

The Helmholtz function is defined as,

$$A = U - TS$$

For an infinitesimal reversible process,

$dA = dU - TdS - SdT,$

and $TdS = dU + PdV$

Hence, $dA = -PdV - SdT$

From this it follows:

(1) For a reversible isothermal process.

$$dA = -PdV$$

or

$$A_f - A_i = \int_i^f P \ dV$$

Hence the change of the Helmholtz function during a reversible isothermal process equals the work done on the system.

2.4. Helmholtz Function.

(2) For a reversible isothermal and isochoric process

$$dA = -PdV$$

or

$$A = constant$$

These properties are of interest in chemistry and are useful in considering chemical reactions that take place isothermally and isochorically. The main importance, however, of the Helmholtz function is its use in statistical mechanics, where it plays a fundamental role. It is possible by statistical methods to calculate the Helmholtz function of some substances as a function of T and V. The equation of state of a substance is then obtained from the relationship.

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

And the entropy from

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

2.5. Gibbs Function

The Gibbs function is defined as

$$G = H - TS$$

For an infinitesimal reversible process,

$$dG = dH - TdS - SdT$$

It will be recalled, however, that

$dH = T\,dS + V\,dP,$

Whence $dG = VdP - SdT$

In the case of a reversible, isothermal, isobaric process

$$dG = 0$$

and $\qquad G = constant$

2.5. Gibbs Function

This is a particularly important result in connection with processes involving a change of phase. Sublimation, fusion, and vaporization take place isothermally and isobarically and can be conceived of as occurring reversibly. *Hence, during such processes, the Gibbs function of the system remains constant.*

If we denote by the symbols g', g'', and g''' the molar Gibbs function of a saturated solid, saturated liquid, and saturated vapor, respectively,

then the equation of the fusion curve is

$$g' = g''$$

the equation of the vaporization curve is

$$g'' = g''',$$

and the equation of the sublimation curve is

$$g' = g'''$$

At the triple point two equations hold simultaneously namely,

$$g' = g'' = g'''$$

All the g's can be regarded as functions of P and T only, and hence the two equations above serve to determine the P and the T of the triple point uniquely.

The Gibbs function is of the utmost importance in chemistry since chemical reactions can be conceived of as taking place at constant P and T. It is also of some use in engineering.

2.6. Names and Symbols for the Thermodynamic Functions

There are many different names and symbols for the thermodynamic functions and therefore unification of symbol of thermodynamic functions are essential.

Practically all authors of modern textbooks are agreed upon the name *entropy* and the symbol *S*.

For the *internal energy* function both *E and U* are used. Since neither *E* nor *U* is ever used to designate any other function, there is no objection in retaining these two letters as alternate symbols.

The symbol for *enthalpy* is almost invariably *H*, but there are three other names that are widely used: heat content, total heat and heat function.

The word "heat" is objectionable for two reasons

(1) The beginner is suitable to receive the erroneous impression that heat in general is a function or that a body has a certain amount of heat in it.

(2) The change in enthalpy is the heat transferred only for an isobaric process. If, for this reason, the *enthalpy* is called the *"heat function at constant pressure"*, then to be consistent, we should have to call *U* the *"heat function for constant volume"*.

2.6. Names and Symbols for the Thermodynamic Functions

Since, however, the process, we should then have as an alternative name for internal energy is equal to work done in an adiabatic process, we should then have as an alternative name for internal energy the *"adiabatic work function"*. Although the idea of assigning to a function a name that suggests a property of the function is an appealing one, the fact remains that the thermodynamic functions have many properties, and it is not satisfactory to choose one property for the purpose of nomenclature.

The situation with regard to the Helmholtz and Gibbs functions is really serious and has let to great confusion and error in calculations, as is shown in the accompanying table.

	Helmholtz function	**Gibbs function**
Most American chemists…	Work function A	Free Energy F
Many physicists…	Free energy F	Thermodynamic Potential G
Compromise suggested by several symbols committees	Helmholtz function A	Gibbs function G

2.7. Two Mathematical Theorems

Theorem 1. If a relation exists among x, y and z, we may imagine z expressed as a function of x and y; hence,

$$dz = \left(\frac{dz}{dx}\right)_y dx + \left(\frac{dz}{dy}\right)_z dy$$

If we let, $M = \left(\frac{dz}{dx}\right)_y$ *and* $N = \left(\frac{dz}{dy}\right)_z$

Then, $dz = \ Mdx + \ Ndy$

Where, z, M and N are all functions of x and y. Differentiating M partially with respect to y and N with respect to x, we get

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{dx\,\partial y}$$

$$\left(\frac{\partial M}{\partial y}\right)_y = \frac{\partial^2 z}{dy\,\partial x}$$

Since the two second derivatives on the right are equal, it follows that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial z}\right)_y$$

This is known as the condition for an exact differential.

Prof. J. K. Baria

2.7. Two Mathematical Theorems

Theorem 2. If a quantity f is a function of x, y and z and a relation exists among x, y and z, then f may be regarded as a function of any two of x, y and z. Similarly any one of x, y and z may be considered to be a function of f and one other of x, y and z. Thus, regarding x to be a function of f and y.

$$dx = \left(\frac{dx}{df}\right)_y df + \left(\frac{dx}{dy}\right)_f dy \qquad ...(1)$$

Considering y to be a function of f and z

$$dy = \left(\frac{dy}{df}\right)_z df + \left(\frac{dy}{dz}\right)_f dz \qquad ...(2)$$

Substituting this expression for dy in the equation (1), we get

$$dx = \left[\left(\frac{dx}{df}\right)_y + \left(\frac{dx}{dy}\right)_f \left(\frac{dy}{df}\right)_z\right] df + \left[\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f\right]_y dz$$

But $\qquad dx = \left(\frac{dx}{df}\right)_z df + \left(\frac{dx}{dz}\right)_f dz$

Equating the dz terms of the last two equations, we get,

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{dy}{dz}\right)_f = \left(\frac{\partial x}{\partial y}\right)_f$$

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

Prof. J. K. Baria

2.8. Maxwell's Equations

A chemical system has been defined as any system of constant mass whose equilibrium states are describable by the 3 thermodynamic coordinates P, V, and T. In describing the behavior of such a system it is convenient to make use of the four functions.

1. The internal energy U.
2. The enthalpy $H = U + PV$.
3. The Helmholtz function $A = U - TS$.
4. The Gibbs function $G = H - TS$.

Any one of these may be regarded as a function of any two of P, V, and T. Suppose for example the both U and S are expressed as functions of V and T, thus.

U = function of (V, T)

And S = function of (V, T)

The second equation may be imagined to be solved for T in terms of S and V; substituting this value of T in the first equation, we should then have

U = function of (S, V)

Consequently we may go further and say that any one of the eight qualities P, V, T, S, U, H, A, and G may be expressed as a function of *any two others*.

2.8. Maxwell's Equations

Now imagine a chemical system undergoing an infinitesimal reversible process from one equilibrium state to another.

1. The internal energy changes by an amount

   $dU = dQ - PdV = TdS - PdV$

   Where U, T and P are all imagined to be functions of S and V.

2. The enthalpy changes by an amounts

   $dH = dU + PdV + VdP = TdS + VdP$

   Where H, T, and V are all imagined to be functions of S and P.

3. The Helmholtz function changes by an amount

   $dA = dU - TdS - SdT = -PdV - SdT$

   Where A, P, and S are all imagined to be functions of V and T.

4. The Gibbs function changes by an amount

   $dG = dH - TdS - SdT = VdP - SdT$

   Where G, V and S are all imagined to be function of P and T.

Since U, H, A, and G are actual functions, their differentials are exact differentials of the type

$$dz = Mdx + Ndy$$

where z, M, and N are all functions of x and y. Therefore

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Applying this result to the four exact differentials dU, dH, dA, and dG

2.8. Maxwell's Equations

$dU = TdS - PdV$	Hence,	$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V$	...(1)
$dH = TdS + VdP$	Hence,	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	...(2)
$dA = -PdV - SdT$	Hence,	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$	...(3)
$dG = VdP - SdT$	Hence,	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$	...(4)

Prof. J. K. Baria

The four equations on the right are known as Maxwell's equations. Maxwell's equations do not refer to a process but merely express relations that hold at any equilibrium of a chemical system.

2.9. First TdS Equation.

The entropy of a chemical system can be imagined as a function of T and V; hence,

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

and

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

But

$T\left(\frac{\partial S}{\partial T}\right)_V = C_V$; And from Maxwell's third equation, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Hence,

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

We shall call the above equation the first TdS equation. It is useful in a variety of ways.

2.9. First TdS Equation.

For example, 1 mole of a van der Waals gas undergoes a reversible isothermal expansion from a volume v_i to a volume $v_{f.}$ How much heat has been transferred?

For 1 mole

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

Using the van der Waals equation of state

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad \text{And} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b}$$

Hence, $TdS = C_V\, dT + RT\,\frac{dv}{v-b}$

Since T is consent, $C_V\, dT = 0$ and, since the process is reversible $q = \int TdS$

$$q = RT\int_{vi}^{vf}\frac{dv}{v-b}$$

And finally,

$$q = RT\ln\frac{v_f - b}{v_i - b}$$

2.10. Second TdS equation.

If the entropy of a chemical system is regarded as a function of T and P, then

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial T}\right)_P dP$$

And $T\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP,$

But $T\left(\frac{\partial S}{\partial T}\right)_P = C_P$

And from Maxwell's fourth equation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

$$TdS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

We shall call the above equation the second TdS equation.

It's two important applications are,

Prof. J. K. Baria

2.10. Second TdS equation.

1. Reversible isothermal change of pressure. When T is constant

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP \text{ and } Q - T\int\left(\frac{\partial V}{\partial T}\right)_P dP$$

Remembering that the coefficient of volume expansion is

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

We obtain $Q = -T\int V\beta\, dP$,

Which can be integrated when the dependence of V and β on the pressure is known. In the case of a solid or liquid, neither V nor β is very sensitive to a change in pressure. For example in the case of mercury, Bridgman found that as the pressure was increased from zero to 1000 atm at 0^0C the volume of 1 mole of mercury changed from 14.72 to 14.67 cm^3, a change of only 1/3 percent and the volume expansivity changed from 181 x 10^{-6} deg^{-1} to 174 x 10^{-6} deg^{-1}, a 4 % change. The volume and the expansivity of most solids and liquids behave similarly, and therefore V and β may be taken out from the integral sign and replaced by average values V and β. We have then

and $Q = -TV\beta\int_{pi}^{pf} dP$, Or $Q = -TV \square\ (P_f - P_i)$,

It is seen from this result that, as the pressure is increased isothermally, heat will flow out of β is positive but, for a substance with a negative expansivity (such as water between 0 and 4^0C) an isothermal increase of pressure causes an absorption of heat.

2.10. Second TdS equation.

If the pressure on 1 mole of mercury at 0^0C is increased reversibly and isothermally from zero to 1000 atm, the heat transferred will be

$$Q = -TV \square \left(P_f - P_i\right)$$

Where T = 273 deg ; V = 14.7 cm^3/mole ; β = 178 x 10^{-6} deg^{-1}; $P_i = 0$

$$Q = -\frac{273 \text{ deg } X\ 14.7\frac{cm^3}{mole}178X10^{-6}\text{ deg}^{-1}\text{ X } 1.013 \text{ X } 10^9 \text{ dynes/Cm}^2}{419\ X\ 10\frac{ergs}{cal}} = -17.3\,\frac{cal}{mole}$$

It is interesting to compare the heat liberated with the work done during the compression.

$$w = \int P \quad dV;$$

but at constant temperature

$dV = \left(\frac{dV}{\partial P}\right)_T \; dP$ And $w = \int \left(\frac{dV}{\partial P}\right)_T \; P\ dP$

Remembering that the isothermal compressibility (Reciprocal of isothermal bulk modulus) is

$$k = -\frac{1}{V}\left(\frac{dV}{\partial P}\right)_T \;,$$

then $w = -\int_{pi}^{pf} VkP \;\; dP$

2.10. Second TdS equation.

The isothermal compressibility is also fairly insensitive to a change of pressure. Bridgman showed that the compressibility of mercury at 0^0C changed from 3.88 x 10^{-12} to 3.79 x 10^{-12} cm^2/dyne (a 2 % change) as the pressure was increased from zero to 1000 atm. We may therefore again replace V and k by average values and obtain

$w = -\frac{vK}{2}\left(P_f^2 - P_i^2\right)$; and taking for mercury : k = 3.84 x 10^{-12} cm^2/ dyne

we get,

$$w = \frac{14.7\frac{\mathrm{cm}^3}{\mathrm{mole}}\, X\, 3.84\ \mathrm{X}\ 10^{-12}\frac{\mathrm{cm}^2}{\mathrm{dyne}}\ \mathrm{X}\ (1.01)^2\ \mathrm{x}\ 10^{18}\left(\frac{\mathrm{dynes}}{cm^2}\right)^2}{2\mathrm{x}\ 4.19\ \mathrm{x}\ 10^7\frac{\mathrm{ergs}}{\mathrm{cal}}} = -0.687\,\frac{cal}{mole}$$

It is seen, therefore that, when the pressure on a mole of mercury at 0^0C is increased from zero to 1000 atm, 17.3 cal of heat is liberated but only 0.687 cal of work is done! The extra amount of heat comes, of course, from the store of internal energy, which has changed by an amount.

$$u_f - u_i = Q - w$$

$$u_f - u_i = 17.3\,\frac{cal}{mole} + 0.687\,\frac{cal}{mole} = -16.6\,\frac{cal}{mole}$$

A similar result is resulted in the case of any substance with a positive expansivitiy. For a substance with a negative expansivity, heat is absorbed and the internal energy is increased.

2.10. Second TdS equation.

2. Reversible Adiabatic Change of Pressure. Since the entropy remains constant.

$$TdS = 0 = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \quad \text{Or } dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP = \frac{TV\beta}{C_P}\,dP$$

In the case of a solid or liquid an increase of pressure of as much as 1000 atm produces only a small temperature change. Also experiment shows that C_P hardly changes even for an increase of 10,000 atm. The above equation, therefore when applied to a solid or a liquid may be written

$$\Delta T = \frac{TV\beta}{C_p}\left(P_f - P_i\right)$$

Where c_P is 6.69 cal/mole.deg. Hence,

$$\Delta T = \frac{273\,\text{deg}\,X\,14.7\,\frac{cm^3}{mole}\,\text{X}\,178\,\text{X}10^{-6}\,deg^{-1}\,X\,1.013\text{ x }10^9\,\frac{\text{dynes}}{\text{cm}^2}}{6.69\,\frac{\text{cal}}{\text{mole deg}}\,X\,4.19\text{ x }10^7\,\frac{\text{ergs}}{\text{cal}}}$$

$$\Delta T = 2.58\,deg$$

2.11. Energy Equation

If a chemical system undergoes an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = TdS - PdV$$

and (the first TdS equation),

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

Combining both equations, we get

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

in which U is imagined as a function of T and V. But

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

and consequently, $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

The above equation, known as the *energy equation*, enables us to draw conclusions about the internal energy of any chemical system whose equation of state is known.

Prof. J. K. Baria

2.11. Energy Equation

1. Ideal Gas

$$P = \frac{nRT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

And $\left(\frac{\partial U}{\partial V}\right)_T = T\,\frac{nR}{V} - P = 0$

Therefore U does not depend on V but is a function of T only.

2. Van der Waals Gas (1 Mole)

$P = \frac{RT}{v-b} - \frac{a}{v^2}$; $\left(\frac{\partial U}{\partial T}\right)_V = \frac{R}{v-b'}$ And $\left(\frac{\partial U}{\partial V}\right)_T = T\,\frac{R}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$

Consequently,

$$dU = C_V\,dT + \frac{a}{v^2}dv$$

and $U = \int c_v\,dT - \frac{a}{v} + const.$

It follows therefore, that the internal energy of a van der Waals gas increase as the volume increases, the temperature remaining constant.

2.12. Difference in Heat Capacities.

Equating the first and second TdS equation.

$$C_P\, dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV;$$

Solving for dT,

$$dT = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V}\, dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}\, dP\,; \qquad But \quad dT = \left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial T}{\partial P}\right)_V dP.$$

$$Therefore \quad \left(\frac{\partial T}{\partial V}\right)_P = \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V} \quad and \quad \left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$$

Both the above equations yield the result that

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_V \qquad but\ we\ know\ that,\ \left(\frac{\partial P}{\partial V}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_V$$

Prof. J. K. Baria

2.12. Difference in Heat Capacities.

This is one of the most important equations of thermodynamics and shows that

1. Since $(\partial P/\partial V)_T$ is always negative for all known substances and $(\partial P/\partial V)_P$ must be positive, then $C_P - C_V$ can never be negative, or C_P can never be less than C_V.
2. As T → 0, $C_P \rightarrow C_V$ or at the absolute zero the two heat capacities are equal.
3. $C_P = C_V$ when $(\partial V/\partial T)_P = 0$ For example, at 4^0C at which density of water is a maximum, $C_P = C_V$.

Laboratory measurements of the heat capacity of solids and liquids usually take place at constant pressure and therefore yield values of C_P. It would be extremely difficult to measure with any degree of accuracy the C_v of a solid or liquid. Values of C_V however, must be known for purposes of comparison with theory. The equation for the difference in the heat capacities is very useful in calculating C_V in terms of C_P and other measurable quantities. Remembering that

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ And $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

We may write the equation in the form

$$C_P - C_V = \left[\frac{TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T}\right]$$

$$C_P - C_V = \frac{TV\,\beta^2}{k}$$

Prof. J. K. Baria

2.12. Difference in Heat Capacities.

As an example of the use of the above equation let us calculate the molar heat capacity at constant volume of mercury at 0^0C and 1 atm pressure. From experiment we have,

$C_p = 6.69$ cal/mole.deg

T = 273 deg

V = 14.72 cm^3/mole

$\beta = 181 \times 10^{-6}\ \text{deg}^{-1}$,

$k = 3.88 \times 10^{-12}\ \text{cm}^2/\text{dyne}$

whence

$$C_P - C_V = \frac{273\ \text{deg x } 14.72 \frac{\text{cm}^2}{\text{mole}}\ X\ (181)^2 \text{ x } 10^{-12}\ \text{deg}^{-2}}{3.88 \text{ x } 10^{-12} \frac{\text{cm}^2}{\text{dyne}}}$$

$$C_P - C_V = 0.809 \frac{\text{cal}}{\text{mole} \cdot \text{deg}}$$

$$\therefore\ C_V = (6.69 - 0.809) \frac{\text{cal}}{\text{mole} \cdot \text{deg}} = 5.88\ \frac{\text{cal}}{\text{mole} \cdot \text{deg}}$$

Finally, $\gamma = \frac{C_P}{C_V} = \frac{6.69}{5.88} = 1.14$

Prof. J. K. Baria

2.13. Ratio of Heat Capacities.

The two TdS equations are

$TdS = C_P\, dT + T\left(\frac{\partial V}{\partial T}\right)_P\, dP$ and $TdS = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_V\, dV$

At constant S,

$C_P\, dT_S = T\left(\frac{\partial V}{\partial T}\right)_P\, dP_S$; and $C_V\, dT_S = -T\left(\frac{\partial P}{\partial T}\right)_V\, dV_S$

Dividing

$$\frac{C_P}{C_V} = -\left[\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial P}{\partial T}\right)_V}\right]\left(\frac{\partial P}{\partial V}\right)_S$$

But the quantity in square brackets is equal to $-\left(\frac{\partial V}{\partial T}\right)_T$

Therefore,

$$\frac{C_P}{C_V} = -\frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T}$$

2.13. Ratio of Heat Capacities.

The adiabatic compressibility is defined as the reciprocal of the adiabatic bulk module or

$k_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$; and, as usual $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$;

We have therefore,

$$\frac{C_p}{C_V} = \gamma = \frac{k}{k_s}$$

From which, k_s may be calculated. In the case of mercury at 0^0C and 1 atm pressure. γ = 1.14, and $k = 3.88 \text{ x } 10^{-12} \frac{\text{cm}^2}{\text{dyne}}$

Whence, $k_s = \frac{3.88 \text{ x } 10^{-12} \frac{\text{cm}^2}{\text{dyne}}}{1.14} = 3.14 \text{ x } 10^{-12} \frac{\text{cm}^2}{\text{dyne}}$

2.14. Expansivity

The volume expansivity of a gas may be calculated from the equation of state or more simply from any empiric equation representing the relation between volume and temperature at constant pressure.

The volume expansivity of liquids and solids is usually calculated from an empirical equation representing the relation between density and temperature at constant pressure. Since the specific volume v is the reciprocal of the density ρ, it follows that

$$\beta = \frac{1}{\rho} \ \frac{\partial \rho}{\partial T}$$

In cases where it is inconvenient or inadvisable to measure the density of a solid over a wide temperature range, the volume expansivity may be calculated from the linear expansivity. Suppose that the three rectangular dimensions of a solid are L_1, L_2, and L_3. Then

$V = L_1 L_2 L_3$

$$\frac{\partial V}{\partial T} = L_2 L_3 \frac{\partial L_1}{\partial T} + L_1 L_3 \frac{\partial L_2}{\partial T} + L_1 L_2 \frac{\partial L_3}{\partial T},$$

$$\frac{1}{V} \frac{\partial V}{\partial T} = \frac{1}{L_1} \frac{\partial L_1}{\partial T} + \frac{1}{L_2} \frac{\partial L_2}{\partial T} + \frac{1}{L_3} \frac{\partial L_3}{\partial T}$$

And $\beta = \alpha_1 + \alpha_2 + \alpha_3$

Where α_1, α_2 and α_3 are the linear expsnsivities along the 3 directions. If the solid is isotropic, then,

$\alpha_1 + \alpha_2 + \alpha_3 = \alpha$

$\beta = 3\alpha$

2.14. Expansivity

There are many methods of measuring the linear expansitivity of solids. If the solid can be obtained in the form of a bar, the simplest method is to make two scratches on the bar and place it horizontally in a temperature bath. The scratches are viewed through separate microscopes, which are mounted on a rigid stand kept at constant temperature. If a change in length $L - L_0$ is produced by a change in the temperature $t - t_0$, then.

$$\alpha = \frac{1}{L_0} \frac{L - L_0}{t - L_0}$$

Where α, the average coefficient, is very nearly equal to the true coefficient when $t - t_0$ is small.

If the linear expansivity of fused quartz is measured by this method, then then expansivity of other materials may be obtained by measuring the expansion relative to quartz. An instrument used for this purpose is the *Abbe-Pulfrich dilatometer*, depicted in fig 2.5 (a). The material B, whose upper surface is plane and well polished, is placed inside a quartz ring A, whose height is a trifle greater than the material. A cover plate C is placed on the quartz ring, and interference fringes are obtained as a result of reflections from the two surfaces close together. The device is made so that the air space between these two surfaces is wedge shaped with an angle that remains constant as both the quartz ring and the material expand.

2.14. Expansivity

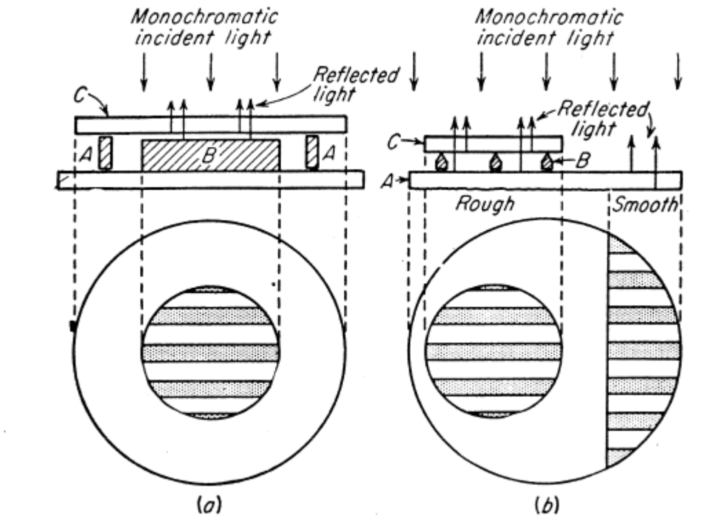


Fig. 2.5 (a) Abbe-Pulfrich dilatometer, (b) Fizeau dilatometer as improved by Merrit

If n fringes travel across the field of view while the temperature changes from t_0 to t, then the optical path difference has changes by nλ, where λ is the wavelength of the light, and the thickness of the air space has changed by nλ/2. If L is the length of the specimen and L_Q that of the quartz, while L_0 is the original length of both the specimen and the quartz ring, then

$$\frac{L_Q - L}{L_0} = \frac{n}{2L_0}$$

If, therefore, $n\lambda/2L_0$ is plotted against t and the slope of the resulting curve is taken at various temperatures, the difference in the expansivities is obtained. Thus

$$\alpha_Q - \alpha = \frac{d}{dt}\left(\frac{n}{2L_0}\right)$$

Another interferometric dilatometer has been developed for high precision work. This experimental arrangement, first suggested by *Fizeau and later developed by Merrit, Austin, Nix, and MacNair at the Bell Telephone Laboratories* is shown in fig. 2.5 (b). Three samples of the material to be studied, B, are cut in the shape of small pyramids a few millimeters high and are used to separate two quartz plates A and C, so that the air space between the plates is wedge shaped. Interference fringes are produced by reflections from the upper surface of A and the lower surface of C, and as the temperature is changed these fringes move across the field of view.

2.14. Expansivity

A small segment of the lower surface of plate A is made smooth, so that interference fringes may be produced by reflections from the upper and lower surfaces of this part of the plate. As the temperature is changed, these fringes also move because of the expansion and changing index of refraction of plate A. By previous calibration the number of these fringes that move may be used to determine the temperature. This part of the apparatus therefore acts as a refraction thermometer. The system is immersed in a specially designed thermostat whose temperature is varied very slowly in a period of as much as 70 hrs., during this time both fringe systems are photographed at regular intervals by an automatically operated motion picture camera. As in the case of the *Pulfrich dilatometer,* the linear expansivity is

$$\alpha = \frac{d}{dt}\left(\frac{n}{2L_0}\right)$$

In order to avoid the delay involved in photographic processing the National Bureau of Standards has developed a photoelectric interferometer in which the movement of interference fringes is detected by a photomultiplier tube and the number of fringes is automatically plotted on a recorder against the measured temperature of the specimen. Thus, all hand operations are eliminated and the data are presented on a chart in a form suitable for immediate determination of expansivities.

In general the volume expansivity of all materials depends on both the temperature and the pressure.

2.14. Expansivity

Temperature Variation of β of ICE and of water

Temp. ^{0}K	Volume Expansivity, 10^{-6} deg^{-1}	Temp. ^{0}K	Volume Expansivity 10^{-6}deg^{-1}
0	0	279	+32
23	-18.3	281	+61
73	+2.4	283	+89
123	+50.4	293	+208
173	+102	303	+304
223	+137	313	+390
273 (solid)	+158	323	+465
273 (liquid)	-67	333	+522
275	-31	343	+586
277	+1	353	+646

2.15. Compressibility

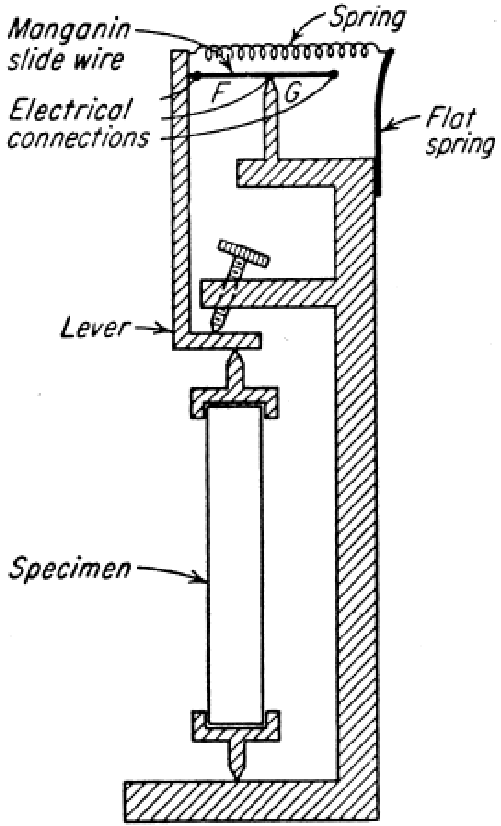


Fig. 2.6. Bridgman piezometer.

The isothermal compressibility of a gas may be calculated from an empiric equation expressing the dependence of V upon P at constant temperature. In the case of solids and liquids the change in volume (or the change in one dimension) produced by a known change in pressure is measured at constant temperature and the average compressibility calculated from the expression.

$$k = -\frac{1}{V_0}\frac{V - V_0}{P - P_0}$$

If the change in pressure is not too large, k is approximately the true isothermal compressibility.

In the apparatus known as a piezometer used by Bridgman for solids, a bar of the solid is contained in a strong iron container filled with oil. The pressure of the oil is varied by a hydrostatic press, and the change in length of the solid relative to that of the iron container is measured by the motion it produces in a high resistance manganin wire, which moves past a contact G, as shown in fig 2.6 . The resistance of the part of the wire between the end F and the fixed contact G is measured with the aid of a potentiometer. The quantity that is measured is the linear compressibility, i.e.

Prof. J. K. Baria

2.15. Compressibility

$$\delta = -\frac{1}{L}\frac{\partial L}{\partial P}$$

If the three rectangular dimensions of the solid are $L_{1,}$ L_2 and L_3, then

$V = L_1 L_2 L_3$

$$\frac{\partial V}{\partial P} = L_2 L_3 \frac{\partial L_1}{\partial P} + L_1 L_3 \frac{\partial L_2}{\partial P} + L_1 L_2 \frac{\partial L_3}{\partial P}$$

$$\frac{1}{V}\frac{\partial V}{\partial P} = \frac{1}{L_1}\frac{\partial L_1}{\partial P} + \frac{1}{L_2}\frac{\partial L_2}{\partial P} + \frac{1}{L_3}\frac{\partial L_3}{\partial P_1}$$

And $k = -\frac{1}{V}\frac{\partial V}{\partial P} = \delta_1 + \delta_2 + \delta_3$

If the solid is isotropic and the δ's are equal and $k = 3\delta$

In general, the isothermal compressibility of all substances is a function of both pressure and temperature.

2.16. Joule Kelvin Effect (Porous plug Experiment).

In the porous plug experiment a gas is made to undergo a continuous throttling process. By means of a pump a constant pressure is maintained on one side of a porous plug and a constant lower pressure on the other side. In the original experiments of Joule and Kelvin a cotton plug was used and the gas flowed through it parallel to the axis of the pipe. In modern measurements a cup of a strong porous material capable of withstanding a large force allows the gas to seep through in a radial direction. Rigid precautions are taken to provide adequate thermal insulation for the plug and the portion of the pipe near the plug. Suitable manometers and thermometers are used to measure the pressure and temperature of the gas on both sides of the plug.

The experiment is performed in the following way: The pressure and temperature on the high pressure side of the plug P_i and T_i are chosen arbitrarily. The pressure on the other side of the plug P_f is then set at any value less than P_i, and the temperature of the gas T_f is measured. P_i and T_i are kept the same, and P_f is changed to another value and the corresponding T_f is measured. This is done for a number of different values of P_f, the corresponding T_f being measured in each case. P_f is the independent variable of the experiment and T_f the dependent variable. The results provide a set of discrete point on T – P diagram, one point being P_iT_i and the others being the various P_f's and T_f'S indicated in **fig.** 2.7. by numbers (1) to (7). Although the points shown in the figure do not refer to any particular gas, they are typical of most gases. It can be seen that, if a throttling process takes place between the states P_iT_i and P_fT_f (3), there is a rise of temperature. Between P_iT_i and P_fT_f (7), however, there is a drop of temperature. In general the temperature change of a gas upon seeping through a porous plug depends on the three quantities P_iT_i and P_f and may be an increase or a decrease or there may be no change whatever.

Prof. J. K. Baria

2.16. Joule Kelvin Effect (Porous plug Experiment).

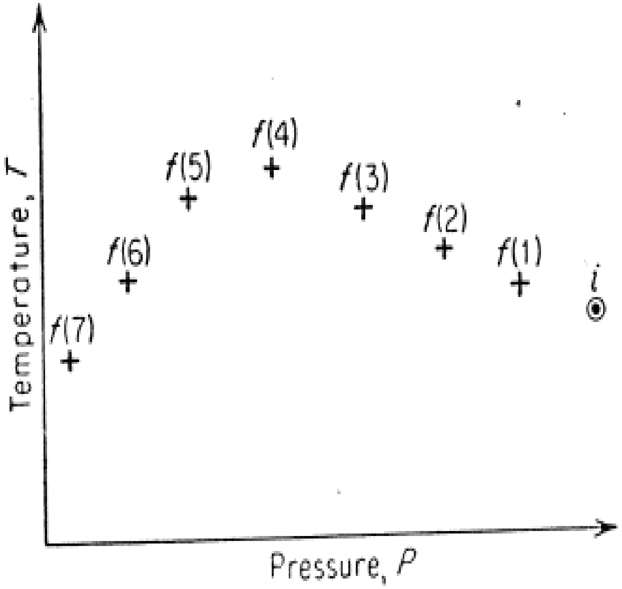


Fig. 2.7. Isenthalpic state of gas.

According to the principle of enthalpy the eight points plotted in **fig. 2.7** represents equilibrium states of some constant mass of the gas, say, 1 gm, at which the gas has the same enthalpy. All equilibrium states of the gas corresponding to this enthalpy must lie on some curve, and it is reasonable to assume that this curve can be obtained by drawing a smooth curve through the discrete points. Such a curve is called an isenthalpic curve. Isenthalpic curve is not the graph of a throttling process. No such graph can be drawn because in any throttling process the intermediate states traversed by a gas cannot be described by means of thermodynamic coordinates. An isenthalpic curve is the locus of all points representing equilibrium states of the same enthalpy. The porous plug experiment is performed to provide a few of these points, the rest being obtained by interpolation.

The temperature on the high pressure side T_i is now changed to another value, P_i being kept the same. P_f is again varied and the corresponding T_f's measured. Upon plotting the new P_iT_i and the new P_f's and T_f's, another discrete set of points is obtained, which determines another isenthalpic curve corresponding to a different enthalpy. In this way a series of isenthalpic curves is obtained. Such a series is shown in **fig.** 2.8. For nitrogen.

2.16. Joule Kelvin Effect (Porous plug Experiment).

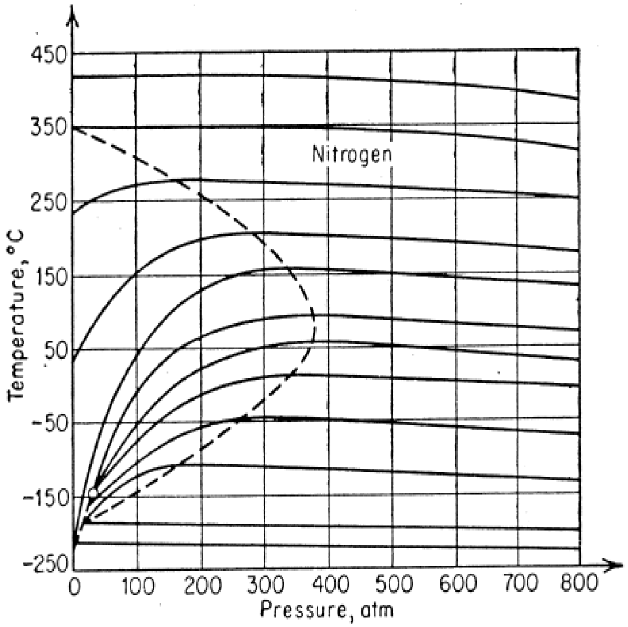


Fig. 2.8. Isenthalpic curve and inversion curve for nitrogen. The encircled point is the critical point (After Roebuck)

The numerical value of the slope of an isenthalpic curve on a T-P diagram at any point is called the Joule – Kelvin co-efficient and will be denoted by μ. Thus,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

The locus of all points at which the Joule Kelvin coefficient is zero. i.e. the locus of the maxima of the isenthalpic curves is known as the inversion curve and is shown in **fig.** 14.2 as a dotted closed curve. The region inside the inversion curve where μ is positive is called the region whereas outside, where μ is negative is the region of heating.

If a vertical line is drawn at some arbitrarily chosen pressure, it will intersect the isenthalpic curves at a number of points at which μ may be obtained by measuring the slopes of the isenthalpics at these points. We should then have a set of values of μ referring to the same pressure but to different temperature. This can then be repeated at another pressure. The data in Table 14.1 were obtained in this way from very careful measurements by *Roebuck and Osterberg.*

2.16. Joule Kelvin Effect (Porous plug Experiment).

Table 4.1 Joule Kelvin Coefficients and Heat Capacities

t, ^{0}C	Helium at 1 atm		Nitrogen at 1 atm	
	Cp, cal/gm. deg	μ, deg/atm	cp, cal/gm.deg	μ, deg/atm
300	1.271	-0.0597	0.2501	+0.0139
200	1.264	-0.0641	0.2490	+0.0558
100	1.257	-0.0638	0.2476	+0.1291
75	1.255	-0.0635	0.2472	+0.1555
50	1.254	-0.0631	0.2469	+0.1854
25	12.52	-0.0624	0.2467	+0.2216
0	1.250	-0.0616	0.2466	+0.2655
-100	1.243	-0.0584	0.2466	+0.6487
-155	1.239	-0.0503	0.2473	+1.449
-180	1.237	-0.0412	0.2480	+2.391

2.16. Joule Kelvin Effect (Porous plug Experiment).

The slope of an isenthalpic curve on a T-P diagram, i.e. the Joule Kelvin Coefficient is

Fig. 2.8 Isenthalpic curves and inversion curves for nitrogen. The encircled point is the critical point.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

In general, the difference in specific enthalpy between two neighboring equilibrium states is

$$dH = TdS + VdP$$

and, according to the second TdS equation,

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

Substituting for TdS, we get

$$dH = C_P dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

or

$$dT = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP + \frac{1}{C_P} dH$$

Prof. J. K. Baria

2.16. Joule Kelvin Effect (Porous plug Experiment).

Regarding T as a function of P and H,

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial h}\right)_P dh$$

whence, since $\mu = \left(\frac{\partial T}{\partial P}\right)_{H,}$

$$\mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

This is the thermodynamic equation for the Joule – Kelvin coefficient. It is evident that, for an ideal gas

$$\mu = \frac{1}{C_P}\left(T\,\frac{R}{P} - V\right) = 0$$

The most important application of the Joule – Kelvin effect is in the liquefaction of gases.