



A pressure cooker cooks vegetables faster at high altitude. (Picture source: <https://pixabay.com/photos/nature-landscape-mountains-4408716/>)

THE THERMODYNAMIC POTENTIALS

Structure

- | | | | |
|------|-------------------------------------|------|-----------------------|
| 10.1 | Introduction | 10.5 | Joule-Thomson Effect |
| | Expected Learning Outcomes | 10.6 | Summary |
| 10.2 | Thermodynamic Potentials | 10.7 | Terminal Questions |
| 10.3 | Maxwell's Relations | 10.8 | Solutions and Answers |
| 10.4 | Deductions from Maxwell's Relations | | |
| | TdS -Equations | | |
| | Energy Equations | | |
| | Clausius-Clapeyron Equation | | |

STUDY GUIDE

In Unit 9, you have learnt the concept of entropy and used it to state the second law of thermodynamics, which emphasises that entropy increases in all natural processes. In this unit, you will learn that a change in a thermodynamic system under specific constraints requires a new function, called *free energy*. We will introduce the concept of *Helmholtz free energy*, F and *Gibbs free energy*, G . In deriving various thermodynamic relations, we shall make extensive use of partial differentiation. Therefore, you should refresh your previous knowledge of this topic. We firmly believe that you must not memorise thermodynamic relations. Instead, you should learn how to obtain these based on mnemonic diagrams. This will make your learning an enjoyable experience. Quite a few numerical problems, solved examples and SAQs based on Maxwell's relations have been given in the unit. Do practice solving these for better understanding. In case, you are not able to solve on your own, read the section again before looking for the solutions provided at the end of the Unit.

“Thermodynamic irreversibility is due to cosmological expansion.”

***Peter T.
Landeberg***

10.1 INTRODUCTION

Helmholtz free energy is also denoted by the symbol A in literature.

So far, we have discussed three thermodynamic functions – temperature (T), internal energy (U), and entropy (S). You may recall that temperature helped us in formulating the equation of state of a thermodynamic system and internal energy enabled us to develop a mathematical formulation of the first law of thermodynamics. The concept of entropy was used to mathematically formulate second law of thermodynamics, which emphasises that entropy increases in all natural processes. From experience, we know that every system has an inherent tendency to approach equilibrium and the first and second laws of thermodynamics do not provide us any information about this. This suggests that there is a need to supplement these laws when we wish to get information about the condition of thermodynamic equilibrium of a system. In Sec. 10.2, you will learn that a change under specific constraints requires a new function, called *free energy*, which is a function of state. We introduce *enthalpy*, H ; *Helmholtz free energy*, F and *Gibbs free energy*, G . The functions U , H , F and G are collectively called *thermodynamic potentials* or *free energies*. You will note that each free energy has its own pair of natural variables. Moreover, these carry a treasure trove of information about the system.

Thermodynamic potentials are very handy in obtaining Maxwell's relations, which are used to derive all important thermodynamic relations. Their usefulness lies in the fact that they frequently relate quantities which seem unrelated. As a result, these relations enable us to link experimental data obtained in different ways or replace a difficult measurement by an easier one. We can also use these to obtain values of one property, which may be straightforward, from calculations or measurement of another property. In brief, these relations are very general and extremely useful as they enormously simplify thermodynamic analysis. You will learn how to derive Maxwell's relations in Sec. 10.3. You will also learn how to obtain TdS -equations and energy equations using Maxwell's relations. We have also discussed applications of Maxwell's relations to derive Clausius-Clapeyron equation in Sec. 10.4. In Sec.10.5, you will learn about Joule-Thomson effect which is used to produce low temperatures.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ define thermodynamic potentials;
- ❖ derive Maxwell's relations from thermodynamic potentials;
- ❖ apply Maxwell's relations to obtain the TdS -equations and energy equations;
- ❖ obtain Clausius-Clapeyron equation from Maxwell's relations;
- ❖ discuss Joule-Thomson effect and how it can be used to produce low temperatures; and
- ❖ define inversion temperature and discuss its importance for liquefaction of gases.

10.2 THERMODYNAMIC POTENTIALS

Consider a gas contained in a cylinder fitted with frictionless piston. The thermodynamic behaviour of this gas can be described in terms of any two variables out of p , V and T ; the third one is automatically fixed in view of the equation of state. Such a system is said to be a **two-coordinate system**. But even for description of such a system, we need several functions of state: p , V , T , S , U and H . (Of these, U and H have dimensions of energy.) In principle, we can construct several functions of state by combining these functions. However, only a few of these may have physical significance. In particular, we define Helmholtz and Gibbs free energies, which also have dimensions of energy like internal energy and enthalpy. As you proceed, you will learn that knowledge of the behaviour of two-coordinate system can be obtained from any one of these four free energies. These are defined as follows:

- Internal energy : U
- Enthalpy : $H = U + pV$
- Helmholtz energy : $F = U - TS = H - pV - TS$
- Gibbs energy : $G = U - TS + pV = F + pV$

(10.1)

It is interesting to mention here that U , H , F and G are collectively referred to as thermodynamic potentials or free energies. Of these, Helmholtz energy is particularly important as it provides a vital connection between thermodynamics and statistical mechanics. That is, it provides a bridge between macroscopic and microscopic viewpoints. You will know these details in Block 4 of this course. Gibbs free energy finds wide applications in the study of phase transitions.

The physical significance of thermodynamic potentials becomes clearer from their differential forms. You will learn about these now.

Differentials of Potential Functions

Let us consider a gaseous system undergoing an infinitesimal reversible process. From Eq. (9.10), you would recall that change in internal energy can be written as

$$dU = TdS - pdV \quad (10.2)$$

Also, a small change in enthalpy, defined as $H = U + pV$, can be written in terms of changes in internal energy, volume and pressure as

$$dH = dU + pdV + Vdp$$

On combining this result with Eq. (10.2), we can write

$$dH = TdS + Vdp \quad (10.3)$$

Likewise, using the definition of Helmholtz free energy ($F = U - TS$), we can write

$$dF = dU - (TdS + SdT)$$

On combining this result with Eq. (10.2), we get

$$dF = -SdT - pdV \quad (10.4)$$

This equation defines the dependence of F on independent variations of T and V . These thermodynamic variables, therefore, constitute the natural pair for Helmholtz energy and we can write $F = F(T, V)$. Note that the right-hand side of Eq. (10.4) comprises two terms and each of these terms consists of a pair of thermodynamic variables such that their product has dimensions of energy.

It readily follows from Eq. (10.4) that entropy and pressure, respectively, of constant V and constant T systems are given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad (10.5a)$$

and
$$p = -\left(\frac{\partial F}{\partial V}\right)_T \quad (10.5b)$$

These relations show that once F is known for a system under consideration, we can obtain complete information about its thermal properties. Further, Eq. (10.5a) shows that the Helmholtz energy decreases with rise in temperature, since entropy of any substance is always positive definite. The higher the entropy of a substance, greater would be the rate of decrease of F . That is why at higher temperatures, the rate of fall of F with temperature is maximum for gases and minimum for solids. Similarly, Eq. (10.5b) shows that an increase in volume decreases Helmholtz energy; the rate of fall being greater at higher pressures.

Starting from the definition of Gibbs energy ($G = F + pV$) and using Eq. (10.4), you can easily convince yourself that an infinitesimal change in G is given by (SAQ 1):

$$dG = -SdT + Vdp \quad (10.6)$$

Note that T and p constitute the pair of natural variables for Gibbs energy and we can write $G = G(T, p)$. Further, we can write

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad (10.7a)$$

and
$$V = \left(\frac{\partial G}{\partial p}\right)_T \quad (10.7b)$$

You should now solve an SAQ before proceeding further.

SAQ 1 – Gibbs energy

Derive Eq. (10.6).

Proceeding further, let us suppose that only one of the free energies is known explicitly. You may then logically ask: Can we get complete information about the system from it? The answer to this question is in the affirmative. We illustrate this by considering the Helmholtz free energy.

To express U, H and G in terms of F , we have to start from their respective definitions. For example, by substituting for S from Eq. (10.5a), the internal energy can be expressed as

$$U = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{F}{T} \right) \right]_V = \left[\frac{\partial (F/T)}{\partial (1/T)} \right]_V \quad (10.8)$$

since $\frac{d}{dT} \left(\frac{1}{T} \right) = -\frac{1}{T^2} dT$.

Eq. (10.8) is known as the **Gibbs-Helmholtz equation**. It finds great use in thermo-chemistry.

Similarly, on substituting for S and p from Eqs. (10.5a) and (10.5b) respectively, you can write

$$H = F + TS + pV = F - T \left(\frac{\partial F}{\partial T} \right)_V - V \left(\frac{\partial F}{\partial V} \right)_T \quad (10.9)$$

and $G = F + pV = F - V \left(\frac{\partial F}{\partial V} \right)_T = -V^2 \left[\frac{\partial}{\partial V} \left(\frac{F}{V} \right) \right]_T = \left[\frac{\partial (F/V)}{\partial (1/V)} \right]_T \quad (10.10)$

Eqs. (10.8), (10.9) and (10.10) clearly show that the entire information about a thermodynamic system can be obtained once we know Helmholtz free energy. You may now logically ask: Can we say the same for other thermodynamic potentials? The answer to this question is in affirmative. However, we will not establish this result. To convince yourself, you should answer the following SAQ.

SAQ 2 – Thermodynamic potentials

- a) Obtain first order derivatives of H and G which justify the following statements:
- At constant entropy, the rate of increase of enthalpy with pressure is greater for a gas than that for a solid.
 - Under isothermal conditions, the Gibbs energy increases more rapidly with pressure for a gas than for a liquid or a solid.
- b) Prove that

i) $p = - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial V} \right)_T$

ii) $H = \left[\frac{\partial (G/T)}{\partial (1/T)} \right]_p$

Before proceeding further, let us recapitulate what you have learnt in this unit so far.

Recap

THERMODYNAMIC FREE ENERGIES

- The behaviour of any pVT system can be explained in terms of four thermodynamic free energies:
 - Internal energy, U
 - Enthalpy, $H = U + pV$
 - Helmholtz energy, $F = U - TS$
 - Gibbs energy, $G = F + pV$
- Each thermodynamic free energy is associated with a natural pair of variables:

$$U = U(S, V); H = H(S, p); F = F(T, V) \text{ and } G = G(T, p)$$

Now that you have learnt about free energies, you can use these to obtain several thermodynamic relations. We first illustrate it by deriving Maxwell's relations. As you proceed, you will learn that these relations derive their usefulness from the fact that they frequently relate quantities, which apparently seem unrelated. Moreover, Maxwell's relations simplify thermodynamic analysis considerably without compromising with elegance.

10.3 MAXWELL'S RELATIONS

You have read about exact differentials in Block 2. We will now use this concept for deriving Maxwell's relations, which connect the partial derivatives of p, V, T and S for a simple compressible substance. These are extremely useful relations. These can be readily applied to determine the changes in a property that cannot be measured directly, by simply measuring the changes in p, V and T .

Suppose z is a function of state which depends on two independent state variables x and y and we can write $z = z(x, y)$. Then an infinitesimal change dz in z due to changes in x and y can be expressed as

$$\begin{aligned} dz &= \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \\ &= Mdx + Ndy \end{aligned} \quad (10.11a)$$

where we have put $M = \left(\frac{\partial z}{\partial x} \right)_y$ and $N = \left(\frac{\partial z}{\partial y} \right)_x$. If we differentiate M with respect to y , keeping x fixed, and N with respect to x , keeping y fixed, we get

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

and

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

We know that the order of differentiation does not affect the value of a perfect differential, that is $\left(\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right)_y$. So, we can write

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad (10.11b)$$

We are now in a position to use Eqs. (10.11a) and (10.11b) to obtain Maxwell relations from thermodynamic potentials. But before doing so, let us summarise what you have learnt in this section.

If dz is an exact differential

$$dz = M dx + N dy$$

where z, M and N are functions of x and y , then

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

To obtain Maxwell's relations using thermodynamic free energies, you can choose any one of the free energies as a function of any two thermodynamic variables out of p, V, S and T . Let us first choose T and V as independent variables. Recall that the free energy associated with these variables is F . It means that we have to refer to Eq. (10.4) and compare it with Eq. (10.11a). You will note that these equations have exactly the same form. In fact, these will be identical if you identify F with z , $-S$ with M , $-p$ with N , T with x and V with y . (This means that F, S and p are now functions of T and V .) Therefore, using Eq. (10.11b), we can write:

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

or
$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (10.12a)$$

Similarly, if we choose T and p as independent variables, we have to consider Gibbs free energy and refer to Eq. (10.6). Then on comparing it with Eq. (10.11a), we note that these equations will become identical if we replace G with z , $-S$ with M , and V with N . Moreover, T is identified with x and p with y . Then using Eq. (10.11b), you will obtain

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \quad (10.12b)$$

Similarly, if we choose S and V and S and p as independent variables, we have to work with Eqs. (10.2) and (10.3), respectively.



Don't forget!

Maxwell's relations can be written from the following statement:

$$\frac{\partial(p, V)}{\partial(x, y)} = \frac{\partial(T, S)}{\partial(x, y)}$$

where x and y can be pairs out of

$$(T, V), (T, p), (S, V)$$

and (S, p) .

The variables occurring at exactly the same position in the numerator as well as the denominator are cancelled out and put as suffix but if they occur in crossed positions, we put a negative sign while cancelling them.

Following the procedure outlined above, you can easily convince yourself that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (10.12c)$$

and
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (10.12d)$$

From Maxwell's relations, you will note that:

- i) Cross multiplication of the variables involved in the partial derivatives always gives the form: $(TS) = (pV)$, which has the dimensions of energy.
- ii) The independent variable of the partial differentiation on the left-hand side appears as a constant on the right-hand side and vice-versa.
- iii) The sign is positive if T appears with p in a partial derivative (remember 'p' for positive).
- iv) We can study pressure and volume variation of entropy in terms of partial derivatives involving extensive and intensive thermodynamic variables

A detailed study of Maxwell's relations leads to a satisfactory explanation of many interesting physical phenomena. For example, let us consider the first Maxwell relation. It can be used to explain the co-existence of two phases of a substance in equilibrium. Similarly, the second relation can be used to explain anomalous expansion of water when it is heated from 0°C to 4°C.

You can perform a very simple activity. Take Indian rubber and stretch it before touching with your lips. Do you experience some heat? We can seek explanation of this and such other phenomena in Maxwell's relations. You will learn about these a little later.

Before you go over to the next section, you should learn how to apply Maxwell's relations. We explain it by solving an example.

EXAMPLE 10.1: MAXWELL'S RELATIONS

Calculate the pressure at which water would boil at 160°C, if the change in specific volume when 1 g of water converted into steam is 1676 cc. Given $1 \text{ cal} = 4.2 \times 10^7 \text{ erg}$, $1 \text{ atm} = 10^6 \text{ dyne cm}^{-2}$ and specific latent heat of vaporization of steam is 540 cal g^{-1} .

SOLUTION ■ From Maxwell's first relation [Eq. (10.12a)], we can write

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

Multiplying both sides by T , we get $T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V$

But we know that $\delta Q = TdS$

$$\therefore \left(\frac{\delta Q}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V$$

Here $\delta Q = ml = 540 \text{ cal} = 540 \times 4.2 \times 10^7 \text{ erg}$,

$T_1 = 100^\circ\text{C} = 373 \text{ K}$, $T_2 = 160^\circ\text{C} = (160 + 273) \text{ K} = 433 \text{ K}$,

$\Delta T = (433 - 373) \text{ K} = 60 \text{ K}$ and $\Delta V = (1676 - 1) \text{ cm}^3 = 1675 \text{ cm}^3$.

Substituting these values in the above relation, we get

$$\begin{aligned} \Delta p &= \frac{\partial T}{T} \left(\frac{\delta Q}{\partial V}\right) = \frac{60 \text{ K} \times 540 \times 4.2 \times 10^7 \text{ erg}}{373 \text{ K} \times 1675 \text{ cm}^3} \\ &= 2.177 \times 10^6 \text{ dyne cm}^{-2} = 2.177 \text{ atm} \end{aligned}$$

Therefore, the required pressure at which water would boil at $160^\circ\text{C} = 2.177 + 1 = 3.177 \text{ atm}$.

This is the working principle of a pressure cooker.

We now summarise the important results of Maxwell's relations.

MAXWELL'S RELATIONS

Recap

- Maxwell's relations help us to study variation of entropy with volume and pressure in terms of partial derivatives involving extensive and intensive variables.
- Four important Maxwell's relations are:

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

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

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

and
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

In the Study Guide of this unit, we emphasized that you should not memorise any thermodynamic relation. We now illustrate how you can conveniently write these down based on a simple sentence.

Do not forget what we have explained in the box ahead.

Memorise the sentence: **Good Physicists Have Studied Under Very Fine Teachers.**

Note that the first letter of each word in this sentence highlights a thermodynamic variable or free energy.

So, we draw a rectangle called mnemonic diagram, whose upper right and lower left corners have been clipped.

Starting from the upper left corner in the figure, place the first letter of each word successively proceeding clockwise, as shown in Fig. 10.1.

Note that each energy function is flanked by its respective set of natural variables.

To write expressions for dG , dH , dU and dF in terms of changes in their natural variables, we choose the energy corner as origin and note the position of natural variables.

If a variable is below or to the left of the origin, a negative sign precedes it. Thus, we can write

$$dG = () dp - () dT$$

The variable in the brackets is chosen such that it ensures dimensions of energy for the product. So, in the instant case, we can write

$$dG = Vdp - SdT$$

You should practice writing expressions for other free energies. Once you have written using the analogy with the relations

$$dz = Mdx + Ndy$$

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

You can obtain Maxwell's relations in the sequence given in the text by working with (T, V) ; (T, p) ; (S, V) and (S, p) with their respective free energies.

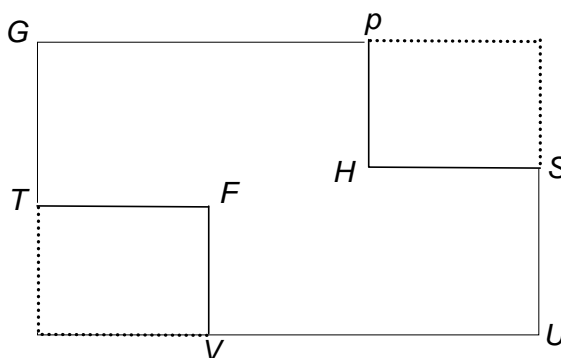
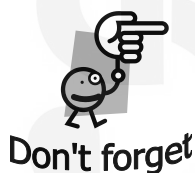


Fig. 10.1: Mnemonic diagram.



10.4 DEDUCTIONS FROM MAXWELL'S RELATIONS

The heat transfer in an infinitesimal reversible process is given by $\delta Q = TdS$. Let us see how Maxwell's relations enable us to calculate heat transfer under different physical conditions.

10.4.1 TdS -Equations

TdS -equations enable us to relate the entropy of a substance with directly measurable quantities, provided its equation of state and heat capacities are known. Depending on the choice of independent variables, we obtain three TdS -equations. To derive the first TdS -equation, let us take T and V as independent variables and express entropy of a substance as

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

An infinitesimal change in T and/or V may induce a corresponding change in entropy. We can mathematically express it as

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

Multiplying throughout by T , we get

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

You would recall that for a gas made up of n moles, $T\left(\frac{\partial S}{\partial T}\right)_V = nC_V$.

Further, using Eq. (10.12a) we replace $\left(\frac{\partial S}{\partial V}\right)_T$ by $\left(\frac{\partial p}{\partial T}\right)_V$. This gives

$$TdS = nC_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV \quad (10.13a)$$

Eq. (10.13a) is called the **first TdS -equation**. Note that

- i) all quantities occurring on the right-hand side of Eq. (10.13a) can be measured, and
- ii) the second term defines pressure variation with temperature for an isochoric process.

So, once we know the equation of state, we can easily determine the pressure variation with temperature at constant volume. (This is explained for a van der Waals' gas in Example 10.2.) However, we can express it as a ratio of two measurable quantities: isothermal compressibility and volume expansivity. We illustrate it now:

Recall that volume expansivity $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ and isothermal compressibility

$$\beta_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \text{ so that } \frac{\alpha}{\beta_T} = -\frac{\left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial V}{\partial p} \right)_T} = -\left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T.$$

The cyclic relation between variables (p, V, T) is

$$\left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial T}{\partial p} \right)_V = -1$$

Using the cyclic relation between thermodynamic variables (p, V, T) we can write

$$\frac{\alpha}{\beta_T} = \left(\frac{\partial p}{\partial T} \right)_V$$

On combining this result with Eq. (10.13a), we can rewrite the first TdS equation as

$$TdS = nC_V dT + T \frac{\alpha}{\beta_T} dV \quad (10.13b)$$

Note that Eqs. (10.13a, b) express variation in entropy in terms of physically measurable quantities. We now illustrate the use of the first TdS equation through an example.

EXAMPLE 10.2: APPLICATION OF MAXWELL'S RELATION

One mole of a van der Waals' gas undergoes a reversible isothermal expansion from a volume v_i to a volume v_f . Calculate the amount of heat transferred in this process.

SOLUTION ■ For one mole, we can write the first TdS equation as

$$TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dv \quad (i)$$

where S, C_V and V , respectively, denote molar entropy, molar heat capacity at constant volume, and molar volume of the gas. For one mole of a van der Waals' gas, we can write the equation of state as:

$$p = \frac{RT}{V-b} - \frac{a}{V^2} \quad (ii)$$

From this, you can easily write: $\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V-b}$ (iii)

Using this result in (i), we get: $Tds = C_V dT + \frac{RT}{V-b} dV$ (iv)

Since the gas undergoes an isothermal expansion, $dT = 0$. Therefore, the first term on the right-hand side of Eq. (iv) drops out. Further, we know that the heat transferred $\delta Q = Tds$. Hence on integrating (iv) over volume between given initial and final values, we get

$$\delta Q = RT \int_{v_i}^{v_f} \frac{dV}{V-b} = RT \ln \left[\frac{V_f - b}{V_i - b} \right] \quad (v)$$

To obtain the second TdS -equation, we take entropy as a function of T and p .

Then we can write:

$$TdS = T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

In terms of heat capacity at constant pressure, we can write

$$TdS = nC_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

If we now use Eq. (10.12b), we get

$$TdS = nC_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp \quad (10.14a)$$

This is the *second* TdS -equation. In terms of volume expansivity α , we can rewrite it as

$$TdS = nC_p dT - TV\alpha dp \quad (10.14b)$$

Similarly, by taking p and V as independent variables and writing $S = S(p, V)$, we get

$$T dS = T \left(\frac{\partial S}{\partial p} \right)_V dp + T \left(\frac{\partial S}{\partial V} \right)_p dV$$

To put it in a more meaningful form, we split the bracketed terms on the RHS of this equation and rewrite it as

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial p} \right)_V dp + T \left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial T}{\partial V} \right)_p dV$$

For n moles of the gas, we can write

$$T dS = nC_V \left(\frac{\partial T}{\partial p} \right)_V dp + nC_p \left(\frac{\partial T}{\partial V} \right)_p dV \quad (10.15)$$

This is the *third* TdS -equation. You may now like to work out an SAQ on TdS -equations.

SAQ 3 – TdS -equations

The pressure on 0.015 litre of mercury at 0°C is increased reversibly isochorically and isothermally from one to 1001 atm. Use Eq. (10.14b) to calculate the heat transfer. It is given that α for mercury = $178 \times 10^{-6} \text{K}^{-1}$. Take $1 \text{atm} = 10^5 \text{Nm}^{-2}$. (Assume that V remains constant.)

EXAMPLE 10.3: APPLICATION OF TdS -EQUATIONS

Write TdS equation for a surface film defined by $TdS = dU - \sigma dA$.

SOLUTION ■ By comparing the TdS equation for surface film with for a hydrostatic system, we note that p and V have been replaced by $-\sigma$ and A , respectively.

Using these variables in the first and second TdS -equations, we can write

$$TdS = C_A dT - T \left(\frac{\partial \sigma}{\partial T} \right)_A dA$$

and

$$TdS = C_\sigma dT + T \left(\frac{\partial A}{\partial T} \right)_\sigma d\sigma$$

Here C_A and C_σ are heat capacities of the film at constant area and at constant surface tension, respectively.

If the film is stretched isothermally and the area increases by dA , the heat transferred to the film is

$$\delta Q_T = TdS = -T \left(\frac{\partial \sigma}{\partial T} \right)_A dA$$

It is an experimentally established fact that surface tension is a function of temperature only. Therefore, we can write

$$\delta Q_T = -T \frac{d\sigma}{dT} dA$$

Since $\frac{d\sigma}{dT}$ is negative for liquids, δQ_T will be positive if $dA > 0$.

Before proceeding further, let us recapitulate what you have learnt in this section so far.

TdS -EQUATIONS

- A TdS -equation helps us to relate changes in entropy in terms of molar heat capacities, volume expansivity and compressibility.
- For a hydrostatic system, the TdS -equations are

$$TdS = nC_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV$$

$$T dS = nC_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$T dS = nC_V \left(\frac{\partial T}{\partial p} \right)_V dp + nC_p \left(\frac{\partial T}{\partial V} \right)_p dV$$

10.4.2 Energy Equations

Just as Maxwell's relations enable us to know heat transfer, we can also use these to study how internal energy changes with volume, temperature or pressure. The resulting relations are known as **energy equations**. To derive first of these, we divide Eq. (10.2) by dV .

This gives $\frac{dU}{dV} = T \frac{dS}{dV} - p$

If T is held constant, the derivatives in the above equation will have to be treated as partial derivatives, so that you can write

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

Using first Maxwell's relation (Eq. (10.12a)), we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad (10.16)$$

Eq. (10.16) is the so-called **first energy equation**.

To illustrate its use, we consider a simple example. For an ideal gas, we know that

$$p = \frac{nRT}{V} \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V}$$

Substituting this in Eq. (10.16), we have

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{nRT}{V} - p = 0$$

This result shows that internal energy of an ideal gas is independent of its volume. So we may say that for an ideal gas U depends on only T . But, in general, U is a function of both T and V . You will understand this by solving the following SAQ.

SAQ 4 – Energy equation

Using Eq. (10.16), show that for one mole of a van der Waals' gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}.$$

The pressure dependence of internal energy can be obtained by dividing Eq. (10.2) by dp and using Eq.(10.12b). The result is the so-called **second energy equation**:

$$\left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T \quad (10.17)$$

Before proceeding further, we would like you to work out an SAQ.

SAQ 5 – Energy equation

Obtain Eq. (10.17) and show that for on ideal gas, internal energy is independent of pressure that U is independent of p .

10.4.3 Clausius-Clapeyron Equation

From the first Maxwell's relation (Eq. (10.12a)) we recall that in isothermal expansion, the heat absorbed per unit volume is equal to the product of the absolute temperature and the rate of increase of pressure with temperature in an isochoric process. Now, let us consider a cylinder which contains a liquid in equilibrium with some of its vapour. (The pressure is called the saturated vapour pressure. It does not depend on the quantities of liquid and vapour present.) If we allow the system to expand at constant temperature, the vapour pressure will stay constant but liquid will evaporate to fill the extra space with vapour. Then we can write $\delta Q = \ell dm$, where ℓ is specific latent heat of evaporation. The change in volume will be equal to $(v_{vap} - v_{liq}) dm$ where v_{vap} and v_{liq} are the specific volumes for the vapour and the liquid, respectively. So, we can rewrite Eq. (10.12a) as

$$\frac{1}{T} \left(\frac{\delta Q}{\delta V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V \quad (10.18a)$$

or
$$\left(\frac{\delta Q}{\delta V} \right)_T = \frac{\ell}{v_{vap} - v_{liq}} = T \left(\frac{\partial p}{\partial T} \right)_V \quad (10.18b)$$

Alternatively, if we hold the volume constant and increase the temperature by dT , the liquid will evaporate till the mixture reaches a new equilibrium state and hence a new saturated vapour pressure. Then we may identify

$$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial p}{\partial T} \right)_{sat}$$

On combining this result with Eq. (10.18b), we can write

$$\left(\frac{\partial p}{\partial T} \right)_{sat} = \frac{\ell}{T[v_{vap} - v_{liq}]} \quad (10.19)$$

This is known as *Clausius-Clapeyron equation*. It is one of the most important formulae in thermodynamics and gives the rate at which vapour pressure must change with temperature for two phases to coexist in equilibrium. (Inversely, you can study the effect of pressure on the boiling point of a liquid.) We can also obtain Eq. (10.19) from the equality of Gibbs Free energies in two co-existing phases. Since $v_{vap} > v_{liq}$ always, $(\partial p / \partial T)_{sat}$ will be positive implying that increase in pressure raises boiling point and vice versa. This explains why vegetables cook faster in a pressure cooker. This also explains why it is difficult to cook food at high altitudes than at the sea level. To give you a feel for the numbers, we may mention that at the top of the Mount Everest, an altitude of about 8 km above the sea level, water boils at about 80°C.

Though we have derived Eq. (10.19) for the evaporation process, the arguments can be extended to any phase change (solid-liquid, liquid-vapour and solid-vapour transition) involving latent heat. That is, Eq. (10.19) applies to all *first order* phase changes in which entropy and volume are

First order phase transition involves change of phase of the matter accompanied by absorption or release of latent heat at constant temperature.

discontinuous at the transition temperature. (You will get an opportunity to arrive at the Clausius-Clapeyron equation based on Gibbs energy in TQ 6.)

The phase diagrams for CO_2 and H_2O are shown in Figs. 10.2a and b, respectively. These curves represent a unique relationship which must hold for two phases to coexist. Note that the three curves intersect at one point. The point (on p - T diagram) where all three phases coexist is known as the *Triple Point*. For CO_2 , $T_{tp} = -56.6^\circ\text{C}$ or 216.4 K and $p_{tp} = 5.11$ atm whereas for water, the triple point is defined by $T_{tp} = 0.0075^\circ\text{C}$ or 273.0075 K and $p_{tp} = 4.58$ atm.

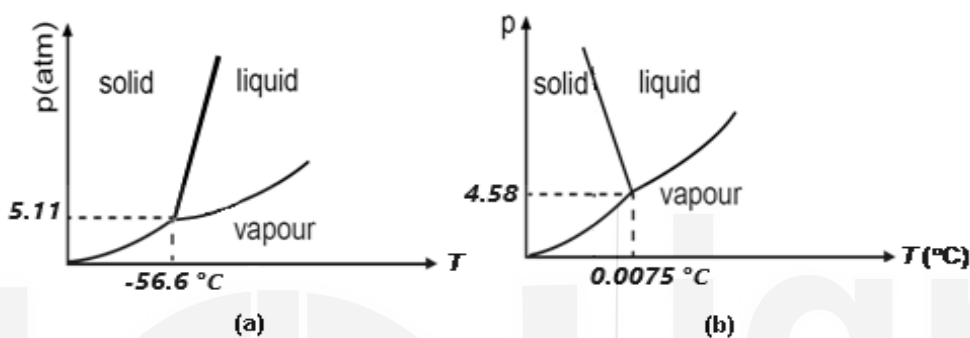


Fig.10.2: The phase diagrams for (a) carbon-di-oxide, and (b) water.

From Fig. 10.2(a) we note that the slope of the solid-liquid curve is positive. This means that most substances expand on melting and dp/dT is positive. So melting point of such materials will increase when pressure is raised. On the other hand, the solid-liquid curve for water (Fig. 10.2b) has a negative slope implying that water expands on freezing and its melting point decreases when pressure increases. Note that water is an exception in that at the triple point, it passes from vapour \rightarrow solid \rightarrow liquid phase when pressure is increased.

It may be remarked here that the Clausius-Clapeyron equation is obeyed by systems to a high degree of accuracy and over a wide range of experimental conditions. This constitutes strong evidence in favour of the second law of thermodynamics.

Now you should study the following example carefully.

EXAMPLE 10.4: CLAUSIUS-CLAYPERON EQUATION

Calculate the change in the melting point of ice at 0°C when pressure is increased by 2 atm. How much pressure is required to lower the melting point by 1°C ? Given, latent heat of fusion is 79.6 cal g^{-1} and the specific volumes of water and ice are 1.001 cm^3 and 1.0908 cm^3 , respectively.

SOLUTION ■ From Eq. (10.19), we can write

$$\left(\frac{\partial p}{\partial T}\right)_{\text{sat}} = \frac{\ell}{T[v_{\text{water}} - v_{\text{ice}}]}$$

On substituting $\ell = 79.6 \times 4.186 \times 10^7 \text{ erg g}^{-1}$, $v_{\text{water}} = 1.0001 \text{ cm}^3$,
 $v_{\text{ice}} = 1.0908 \text{ cm}^3$ and $T = 273.16 \text{ K}$, we get

$$\frac{dp}{dT} = \frac{79.6 \times 4.186 \times 10^7 \text{ erg g}^{-1}}{(273.16 \text{ K}) \times (1.0001 - 1.0908) \text{ cm}^3} = -13.45 \times 10^7 \text{ dyne cm}^{-2} \text{ K}^{-1}$$

Since $dp = 2 \text{ atm} = 2.026 \times 10^6 \text{ dyne cm}^{-2}$, the change in melting point is given by

$$dT = -\frac{2.026 \times 10^6 \text{ dyne cm}^{-2}}{13.45 \times 10^7 \text{ dyne cm}^{-2} \text{ K}^{-1}} = -0.015 \text{ K} = -0.015^\circ \text{C}$$

This result shows that the melting point of ice decreases with pressure; the drop per atmosphere being 0.0075°C . Thus, when enough pressure is applied, ice melts. This fact is of significance in the game of ice skating as well as in the study of glaciers.

The increase in pressure required to lower the melting point of ice by 1°C is $1 \text{ K} / 0.0075 \approx 133 \text{ atm}$.

10.5 JOULE-THOMSON EFFECT

From the discussion of van der Waals' equation in Block 1, you may recall that in arriving at his equation, van der Waals assumed that gas molecules have finite size and experience molecular attraction. To verify these assumptions, Joule performed a simple experiment wherein he allowed a gas to undergo free expansion. He argued that if intermolecular forces do exist, some work will be done against these when a gas expands. And since this work can only be done at the expense of the internal energy of the gas, its temperature should drop producing a cooling effect. However, he could observe no cooling effect.

Soon after, Joule carried out a series of experiments in collaboration with Thomson. They made a gas to **expand adiabatically through a porous plug from a constant higher pressure to a constant lower pressure**. They showed that when temperature of the gas was below a certain temperature, known as inversion temperature, it did show cooling effect. This is known as **Joule-Thomson effect**. The findings of Joule-Thomson experiment are summarized below:

- All gases showed a change in temperature after passing through the porous plug.
- At ordinary temperatures, all gases, except hydrogen and helium, showed cooling effect. In fact, these gases showed slight heating, which was completely unexpected.
- At low enough temperatures, all gases showed cooling effect.
- The fall in temperature was directly proportional to the pressure difference on the two sides of the porous plug. However, for a given difference of

pressure, the drop in temperature was more if the initial temperature of the gas was less.

- For every gas, no change in temperature was observed when it was made to expand at the temperature of inversion, denoted as T_i . When the initial temperature of a gas was below the temperature of inversion, it cooled after adiabatic expansion through the porous plug.

Joule-Thomson coefficient is defined as

$$\mu = \frac{\Delta T}{\Delta p} \quad (10.20)$$

Without going into details, we will just quote the result for a van der Waals' gas:

$$\mu = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) \quad (10.21)$$

We know that Δp is greater than zero since gas is made to expand from a constant higher pressure to a constant lower pressure. So, Eq. (10.21) suggests that cooling or heating in Joule-Thomson expansion will be determined by the competition between terms characterizing intermolecular forces represented by a and finite size of gas molecules represented by b .

If intermolecular forces are strong, i.e. $a \gg b$, then $\left(\frac{2a}{RT} - b \right) > 0$.

Hence, $\Delta T > 0$ and the gas will cool and vice versa. However, there will be neither cooling nor heating if

$$\frac{2a}{RT_i} = b \quad (10.22)$$

T_i is referred to as *inversion temperature*. It signifies that when a gas undergoes Joule-Thomson expansion below its *inversion temperature*, it will cool down. But if the temperature before expansion is above its *inversion temperature*, it will warm up.

The inversion temperatures for some typical gases are given in Table 10.1.

Table 10.1: Inversion temperatures of some gases

Gas	He	H ₂	N ₂	A	O ₂	CO ₂	Air
T_i (K)	23.6	195	621	723	893	1500	603

Note that for H₂ and He, T_i is well below the room temperature (273K) and that is why they show warming at ordinary temperatures.

From Eq. (10.21) we further note that for a perfect gas, $a = b = 0$. It means that Joule-Thomson coefficient for a perfect gas would be zero.

We now sum up what you have learnt in this unit.

10.6 SUMMARY

Concept	Description
Thermodynamic potentials	<ul style="list-style-type: none"> ■ When a system can be subjected to work by pressure only, there exist four thermodynamic potential functions: internal energy U; enthalpy $H = U + pV$; Helmholtz function $F = U - TS$; and Gibbs function $G = U - TS + pV$. ■ Infinitesimal changes in thermodynamic potentials are given by $dU = TdS - pdV, \quad dH = TdS + Vdp$ $dF = -SdT - pdV, \quad dG = -SdT + Vdp$
Maxwell's relations	<ul style="list-style-type: none"> ■ The four Maxwell's relations are $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$ $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$
TdS-equations	<ul style="list-style-type: none"> ■ Three TdS-equations relate changes in entropy to change in temperature, volume or pressure: $TdS = nC_V dT + T \left(\frac{\partial p}{\partial T}\right)_V dV$ $TdS = nC_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dV$ $TdS = nC_V \left(\frac{\partial T}{\partial p}\right)_V dp + nC_p \left(\frac{\partial T}{\partial V}\right)_p dV$
Energy equations	<ul style="list-style-type: none"> ■ Energy equations specify the variation of internal energy with volume and pressure: $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$ $\left(\frac{\partial U}{\partial p}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_p - p \left(\frac{\partial V}{\partial p}\right)_T$

Joule-Thomson coefficient

■ Joule-Thomson coefficient is defined as

$$\mu = \frac{\Delta T}{\Delta p} = \frac{1}{C_p} \left(\frac{2a}{RT} - b \right) = \frac{b}{C_p} \left(\frac{T_i}{T} - 1 \right)$$

where $T_i = \frac{2a}{Rb}$ is the temperature of inversion of the gas. Every gas undergoing Joule-Thomson expansion at a temperature below the inversion temperature cools down and vice versa.

10.7 TERMINAL QUESTIONS

1. For a magnetic system, the infinitesimal change in internal energy may be expressed as

$$dU = TdS + VB dM$$

Here B is the applied magnetic field and M is the intensity of magnetisation. If $M = \frac{m'}{V}$ where m' is the magnetic moment, you can write

$$dU = TdS + B dm'$$

Now, starting from the above equation, write for the magnetic system

- the four Maxwell's relations,
 - the second TdS -equation.
2. A gas obeys the equation $p(V - b) = RT$, where b is constant. Show that
- U is a function of only T ,
 - $p(V - b)^\gamma = \text{constant}$ for the gas undergoing a reversible adiabatic process.
3. For an ideal gas show that
- coefficient of volume expansion is a function of only temperature.
 - the isothermal compressibility is a function of only pressure.
4. Water boils at a temperature of 101°C at a pressure of 78.8 cm of Hg. If 1 g of water occupies 1601 cm^3 on evaporation, calculate the latent heat of steam. Given $1 \text{ cal} = 4.2 \times 10^7 \text{ erg}$ and $g = 980 \text{ cm s}^{-2}$.
5. Calculate the specific volume of solid sulphur from the following data: Melting point of sulphur = 115°C ; latent heat of fusion of sulphur = 9.3 cal g^{-1} , volume of 1 g of liquid sulphur = 0.513 cm^3 ; rate of change of melting point with pressure is $0.025^\circ\text{C atm}^{-1}$. ($1 \text{ atm} = 10^6 \text{ dyne cm}^{-2}$)
6. When two phases of a substance co-exist in equilibrium at constant temperature and pressure, their specific Gibbs free energies are equal. Using this fact, obtain Clausius-Clapeyron equation.

10.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. We know that $G = F + pV$

$$\therefore dG = dF + pdV + Vdp = -SdT - pdV + pdV + Vdp$$

$$\text{or } dG = -SdT + Vdp, \text{ which is Eq. (10.6).}$$

$$2. \text{ a) i) From Eq. (10.3), we can write } V = \left(\frac{\partial H}{\partial p} \right)_S$$

For a fixed mass, a gas occupies more space (volume) than a solid. So, at constant entropy, the rate of increase of enthalpy with pressure is greater for a gas than a solid.

$$\text{ii) From Eq. (10.7b), we recall that } V = \left(\frac{\partial G}{\partial p} \right)_T$$

As explained above, we can say that at constant temperature, Gibbs energy increases with pressure more rapidly for a gas than that for a liquid or a solid.

$$\text{b) i) From Eq. (10.5b), we know that } p = - \left(\frac{\partial F}{\partial V} \right)_T$$

On substituting for F from Eq. (10.1), we get

$$p = - \left[\frac{\partial}{\partial V} (U - TS) \right]_T = - \left(\frac{\partial U}{\partial V} \right)_T + T \left(\frac{\partial S}{\partial V} \right)_T$$

This relation signifies that pressure exerted by a system arises out of two contributions: isothermal variations of internal energy and entropy with volume. While the first term dominates in case of solids, the second term is more prominent in elastic polymers such as rubber. The variation of entropy of a system with volume may also contribute to pressure when its energy remains constant. This is exactly what happens in the case of an ideal gas at constant temperature.

$$\text{ii) We know that } G = H - TS \text{ and } S = - \left(\frac{\partial G}{\partial T} \right)_p. \text{ Therefore, we can}$$

$$\text{invert this relation to write } H = G - T \left(\frac{\partial G}{\partial T} \right)_p$$

On multiplying and dividing by T^2 , we rewrite it as

$$= T^2 \left[\frac{G - T \left(\frac{\partial G}{\partial T} \right)_p}{T^2} \right] = T^2 \left[\frac{G}{T^2} - \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p \right] = -T^2 \left[\frac{\partial}{\partial T} \left(\frac{G}{T} \right) \right]_p$$

$$\text{But } \left[\frac{\partial}{\partial T} \left(\frac{1}{T} \right) \right]_p = -\frac{1}{T^2}. \text{ Hence, we get the desired result:}$$

$$H = \left[\frac{\partial (G/T)}{\partial (1/T)} \right]_p$$

3. Since the process is reversible and isothermal ($dT = 0$), from Eq. (10.14) we have

$$\delta Q = TdS = -T \left(\frac{\partial V}{\partial T} \right)_p dp = -TV\alpha dp \quad (i)$$

$$\therefore Q = -\int TV\alpha dp = -T \int V\alpha dp \quad (\because T \text{ is a constant})$$

Since V and α remain constant during the process, we can write

$$Q = -TV\alpha \int dp = -TV\alpha(p_f - p_i) \quad (ii)$$

where p_i and p_f are the initial and the final pressures.

We are given that $T = (0 + 273)\text{K} = 273\text{K}$, $V = 0.015$ litre,
 $\beta = 178 \times 10^{-6}\text{K}^{-1}$, $p_f = 1001$ atm, and $p_i = 1$ atm,

On substituting these values in Eq. (ii), we get

$$Q = -(273\text{K}) \times (0.015 \text{ litre}) \times (178 \times 10^{-6}\text{K}^{-1}) \times (1000 \text{ atm}) \\ = -0.729 \text{ litre atm}$$

Since $1 \text{ litre} = 10^{-3} \text{ m}^3$, and $1 \text{ atm} = 10^5 \text{ Nm}^{-2}$ we can express this result as

$$Q = -0.729 \times (10^{-3} \text{ m}^3) \times 10^5 \text{ Nm}^{-2} = -72.9 \text{ Nm} = -72.9 \frac{\text{J}}{4.2 \text{ Jcal}^{-1}} \\ = -17.4 \text{ cal}$$

The negative sign signifies that heat flows out of the system during the above process.

4. For one mole of a van der Waals' gas, we have $p = \frac{RT}{V-b} - \frac{a}{V^2}$

and $\left(\frac{\partial p}{\partial T} \right)_p = \frac{R}{V-b}$

From Eq. (10.12), we have $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p$

On substituting for p and $(\partial p / \partial T)_v$, we get

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

5. From Eq. (10.2) we recall that $dU = TdS - pdV$

Dividing both sides by dp , we can write for constant T

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

On using Eq. (10.13), we get

$$\left(\frac{\partial U}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p - p \left(\frac{\partial V}{\partial p} \right)_T$$

For an ideal gas,

$$pV = nRT$$

or $V = \frac{nRT}{p}$, so that $\left(\frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}$ and $\left(\frac{\partial V}{\partial p} \right)_T = -\frac{nRT}{p^2}$

$$\therefore \left(\frac{\partial U}{\partial p} \right)_T = -\frac{nRT}{p} - p \left(-\frac{nRT}{p^2} \right) = 0$$

This result shows that internal energy of an ideal gas is independent of pressure.

Terminal Questions

1. a) We have $dU = TdS + Bdm'$

If we compare this with Eq. (10.2a), we see that p has been replaced by B and V by $-m'$. Using this idea, we may write the analogues of Eq. (10.2) for magnetic system as follows:

$$dU = T dS + B dm'$$

$$dH = T dS - m' dB$$

$$dF = -S dT + B dm'$$

$$dG = -S dT - m' dB$$

Now applying the conditions (10.13), we have the following four Maxwell's relations

$$\left(\frac{\partial T}{\partial m'} \right)_S = \left(\frac{\partial B}{\partial S} \right)_{m'}$$

$$\left(\frac{\partial T}{\partial B} \right)_S = - \left(\frac{\partial m'}{\partial S} \right)_B$$

$$\left(\frac{\partial S}{\partial m'} \right)_T = - \left(\frac{\partial B}{\partial T} \right)_{m'}$$

$$\left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial m'}{\partial T} \right)_B$$

- b) The TdS -equation may also be obtained by replacing p by B and V by $-m'$. Thus, from Eq. (10.14a), we have $T dS = V C_{Bd}dT + T \left(\frac{\partial m'}{\partial T} \right)_B dB$

2. a) $p(V-b) = RT$ and so, $p = \frac{RT}{V-b}$ and $\left(\frac{\partial p}{\partial T} \right)_V = \frac{R}{V-b}$

We know from Eq. (10.16), that

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_V - p = \frac{RT}{V-b} - p = p - p = 0$$

So, u is a function of only T .

- b) We know from Eqs. (10.13 and 10.14) that $TdS = C_V dT + T \left(\frac{\partial p}{\partial T} \right)_V dV$

$$\text{and } TdS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp$$

For a reversible adiabatic process, $TdS = 0$

$$\therefore C_V dT = -T \left(\frac{\partial p}{\partial T} \right)_V dV \quad \text{and} \quad C_p dT = T \left(\frac{\partial V}{\partial T} \right)_p dp$$

$$\text{or } C_V dT = -\frac{RT}{V-b} \quad \text{and} \quad C_p dT = \frac{RT}{p} dp$$

$$\text{Hence, } \frac{C_p dT}{C_V dT} = \frac{\frac{RT}{p} dp}{-\frac{RT}{V-b} dV} = -\frac{V-b}{p} \frac{dp}{dV} = \gamma$$

$$\text{so that } -\gamma \frac{dV}{V-b} = \frac{dp}{p}$$

On integrating both sides, we can write

$$-\gamma \ln(V-b) = \ln p + K$$

where K is constant of integration. We can rewrite it as

$$\ln(p(V-b)^\gamma) = K$$

On taking antilog of both sides, we get $p(V-b)^\gamma = K'$

3. i) The coefficient of volume expansion or volume expansivity is given as

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \quad \text{For an ideal gas, } pV = RT$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{p} \quad \text{or} \quad \beta = \frac{1}{V} \frac{R}{p} = \frac{1}{T}$$

That is coefficient of volume expansion of an ideal gas is an inverse function of temperature only.

- ii) The expression for thermal compressibility is written as

$$\alpha = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left(-\frac{RT}{p^2} \right) = \frac{1}{p}$$

This shows that the isothermal compressibility of an ideal gas is a function of pressure only.

4. From Clausius Clapeyron equation, we know that

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)} \quad \Rightarrow \quad \ell = T(v_2 - v_1) \frac{dp}{dT}$$

$$\text{Here } T = 373\text{K}, \quad v_2 - v_1 = 1600\text{cm}^3 \text{ g}^{-1}$$

$$dp = (78.8 - 76.0) \text{ cm} \times (13.6 \text{ g cm}^{-3}) \times (980 \text{ cm s}^{-2}) = 37318 \text{ dyne cm}^{-2}$$

and $dT = 1\text{K} = 1^\circ\text{C}$

$$\therefore \ell = \frac{(373\text{K}) \times 1600\text{cm}^3\text{g}^{-1} \times (37318\text{dyne cm}^{-2})}{1\text{K}} = 22.27 \times 10^9 \text{ ergg}^{-1}$$

$$= \frac{22.27 \times 10^9 \text{ ergg}^{-1}}{4.2 \times 10^7 \text{ ergcal}^{-1}} = 530.2 \text{ cal g}^{-1}$$

5. From Clausius-Clapeyron equation, we know that

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)}$$

$$\text{or } (v_2 - v_1) = \frac{\ell}{T} \frac{dT}{dp}$$

$$\text{Here } \frac{dT}{dp} = 0.025 \text{ K atm}^{-1}, \ell = 9.3 \text{ cal g}^{-1} \text{ and } T = 388 \text{ K}$$

$$\therefore (v_2 - v_1) = \frac{9.3 \text{ cal g}^{-1}}{388 \text{ K}} \times 0.025 \text{ K atm}^{-1} = 0.252 \text{ cm}^3$$

Since the volume of liquid sulphur is $v_2 = 0.513 \text{ cm}^3$, the volume of solid sulphur is given by

$$v_1 \equiv V_s = (0.513 - 0.252) \text{ cm}^3 = 0.261 \text{ cm}^3.$$

6. The specific Gibbs free energy of two phases must always be equal for coexistence of first order phase transitions: $g_1 = g_2$ (i)

If we change the temperature and pressure by ΔT and Δp , respectively, there will be a corresponding change in specific Gibbs free energies as well. But the condition for two phases to co-exist and be stable is given by

$$g_1 + \Delta g_1 = g_2 + \Delta g_2 \quad (\text{ii})$$

From Eqs. (i) and (ii), we can write $\Delta g_1 = \Delta g_2$.

That is, the change in the specific Gibbs free energy of one phase in equilibrium with another phase is equal to the change in specific Gibbs free energy of the other phase. For one-component system, which can exist in two phases, the specific Gibbs energy is given by

$dg = -sdT + vdp$. So, on substituting for Δg_1 and Δg_2 , we get

$$v_1 \Delta p - s_1 \Delta T = v_2 \Delta p - s_2 \Delta T$$

$$\text{or } \frac{\Delta p}{\Delta T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}$$

where Δs and Δv , respectively, denote changes in specific entropy and specific volume when the system goes from one phase to another. If the specific latent heat (absorbed) required to accomplish change from phase 1 to phase 2 is ℓ , we can write

$$s_2 - s_1 = \frac{\ell}{T}$$

Hence, the required relation for changes in pressure and temperature in stable phase equilibrium is

$$\frac{dp}{dT} = \frac{\ell}{T(v_2 - v_1)}$$

This is the Clausius-Clapeyron equation. It gives the rate at which pressure must change with temperature for two phases to remain in equilibrium.

(Note: For details about the phase transitions, you should consult books mentioned in Further Readings at the end of this block.)