

MODULE 3

Unit 1	Combined First and Second Laws
Unit 2	Thermodynamic Potentials
Unit 3	The Maxwell Relations of Thermodynamics
Unit 4	TdS Equations

UNIT 1 COMBINED FIRST AND SECOND LAWS**CONTENTS**

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1.0 INTRODUCTION

The first and second laws of thermodynamics can be combined to obtain very important thermodynamics relations.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- write the equation for combined first and second laws of thermodynamics; and
- derive some useful thermodynamics relations from the combine first and second laws.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.

3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Combined First and Second Laws of Thermodynamics

The first law of Thermodynamics is

$$dQ = dU + dW \quad 10.1$$

And the second law of thermodynamics is

$$dQ = TdS \quad 10.2$$

but differential work

$$dW = PdV \quad 10.3$$

The combination of these three equations in any infinitesimal reversible process, for a PVT system gives

$$TdS = dU + PdV \quad 10.4$$

Equation 10.4 is the combined form of the first and second laws of thermodynamics for a PVT system. Some useful thermodynamics relations can be derived from equation 10.4 by selecting T and V, T and P, P and V as independent variables. It is important to note that the state of a pure substance (Module 1 Unit 1) can be defined or specified by any two of its properties.

3.2 T and V Independent

From equation 10.4

$$dS = \frac{1}{T}(dU + PdV) \quad 10.5$$

Consider the internal energy U as a function of T and V , i.e. $U(T, V)$, then the derivative of U is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad 10.6$$

Put equation 10.6 in 10.5

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV \quad 10.7$$

Also consider entropy S as function of two independent variables T and V , i.e. $S(T, V)$, then the derivative of S is

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad 10.8$$

By comparing equation 10.7 with 10.8 (or equate 10.7 and 10.8), we obtain

$$\frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial S}{\partial T} \right)_V \quad 10.9$$

and

$$\frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] = \left(\frac{\partial S}{\partial V} \right)_T \quad 10.10$$

If we differentiate equation 10.9 partially with respect to V at constant T and differentiate 10.10 partially with respect to T and constant V , equating the mixed second-order partial derivatives of S gives

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P \quad 10.11$$

It can be shown that (check SEA1 in module 3, unit 4) $\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k}$,

therefore, equation 10.11 becomes

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{T\beta}{k} - P \quad 10.12$$

Equations 10.11 and 10.12 show the dependence of the internal energy of a system on volume, at constant temperature and this can be calculated from the equation of state (i.e. using equation 10.11), or from the values of β , κ , T and P (i.e. using equation 10.12).

Recall from module 2, unit 2 under consequences of the first law of thermodynamics that

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (\text{i.e. equation 6.7})$$

By making use of equation 10.11, we have

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = \frac{\beta^2 T V}{\kappa} \quad 10.13$$

Thus the difference ($C_P - C_V$) can be calculated for any substance, from equation of state or from values of \mathbf{T} , \mathbf{V} , β and κ .

SELF ASSESSMENT EXERCISE 1

- i. Derive equation 10.11 from equation 10.9 and 10.10
- ii. Find $C_P - C_V$ for a certain gas whose equation of state $(P + b)V = nRT$.
- iii. We know that $\left(\frac{\partial U}{\partial T} \right)_V = C_V$, put this and equation 10.11 in 10.6 to obtain

$$dU = C_V dT + [T \left(\frac{\partial P}{\partial T} \right)_V - P] dV \quad 10.13$$

3.3 T and P Independent

In terms of enthalpy $H = U + PV$, equation 10.4 can be rewritten as

$$dS = \frac{1}{T} (dH - V dP) \quad 10.14$$

Check block 1 for how we arrived at 10.14

Consider the enthalpy \mathbf{H} as a function of \mathbf{T} and \mathbf{P} , i.e. $\mathbf{H}(\mathbf{T}, \mathbf{P})$, then the derivative of \mathbf{H} is

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad 10.15$$

Put equation 10.15 in 10.14, then

$$dS = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT + \frac{1}{T} \left[\left(\frac{\partial H}{\partial P} \right)_T - V \right] dP \quad 10.16$$

Also consider entropy \mathbf{S} as function of two independent variables \mathbf{T} and \mathbf{P} , i.e. $\mathbf{S}(\mathbf{T}, \mathbf{P})$, then the derivative of \mathbf{S} is

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad 10.17$$

By comparing equation 10.16 with 10.17, we obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T}\right)_P, \quad 10.18$$

and

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]. \quad 10.19$$

If we differentiate equation 10.18 partially with respect to \mathbf{P} at constant \mathbf{T} and differentiate 10.19 partially with respect to \mathbf{T} and constant \mathbf{P} , equating the mixed second-order partial derivatives of \mathbf{S} gives

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V \quad 10.20$$

From using equation 5.13, $\left(\frac{\partial V}{\partial T}\right)_P = \beta V$, then

$$\left(\frac{\partial H}{\partial P}\right)_T = -\beta VT + V \quad 10.21$$

Equation 10.21 is similar to equation 10.12. It shows the dependence of enthalpy on pressure, at constant temperature and this can be calculated from the equation of state (i.e. from equation 10.20), or from the values of β , \mathbf{T} and \mathbf{V} (i.e. from equation 10.21).

Also since we know that $\left(\frac{\partial H}{\partial T}\right)_P = C_P$, put this and equation 10.20 in equation 10.15 to have

$$dH = C_P dT - \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] dP \quad 10.22$$

Block 1

Enthalpy $H=U + PV$

Derivative of H gives

$$dH = dU + PdV + VdP$$

make dU subject of the expression

$$dU = dH - PdV - VdP \quad *$$

$$\text{but } dS = \frac{1}{T} (dU + PdV) \quad **$$

put equation (*) in (**) gives

$$dS = \frac{1}{T} (dH - PdV - VdP + PdV)$$

Then,

$$dS = \frac{1}{T} (dH - VdP)$$

3.4 P and V Independent

Consider entropy S as a function of P and V , i.e. $S(P, V)$, derivative of S is

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV \quad 10.23$$

Also consider internal energy U as a function of P and V , i.e. $U(P, V)$, the derivative of U is

$$dU = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \quad 10.24$$

Put equation 10.23 in 10.5

$$dS = \frac{1}{T} \left(\left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV + PdV \right)$$

Rearrange to get

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_P + \frac{P}{T} \right] dV \quad 10.25$$

By comparing equation 10.23 with 10.25, we obtain

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial P}\right)_V \quad 10.26$$

and

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_P + \frac{P}{T} \quad 10.27$$

$\left(\frac{\partial U}{\partial P}\right)_V$ can be written as $\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$ (i.e. chain rule of partial derivatives) then equation 10.26 becomes

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \quad 10.28$$

But

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V, \text{ and } \left(\frac{\partial T}{\partial P}\right)_V = \frac{\kappa}{\beta} \quad 10.29$$

Put equation 10.29 in 10.28 to give

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{C_V}{T} \frac{\kappa}{\beta} \quad 10.30$$

Equation 10.30 gives the change in entropy with respect to pressure at constant volume $(\frac{\partial S}{\partial P})_V$ in terms of measurable quantities C_V , k , β , and T .

4.0 CONCLUSION

We have derived in this unit, some useful relations from the combined first and second laws of thermodynamics.

5.0 SUMMARY

In this unit, you have learnt that:

- the combined first and second laws of thermodynamics is $TdS=dU + PdV$
- the variation in enthalpy with respect to pressure at constant temperature is $(\frac{\partial H}{\partial P})_T = -\beta VT + V$
- the difference between the specific heat capacities from combined first and second law is $C_P - C_V = T(\frac{\partial P}{\partial T})_V(\frac{\partial V}{\partial T})_P = \frac{\beta^2 TV}{k}$
- the variation in entropy with pressure at constant volume is $(\frac{\partial S}{\partial P})_V = \frac{C_V}{T} \frac{\kappa}{\beta}$.

6.0 TUTOR-MARKED ASSIGNMENT

1. Write the equation for combined first and second law of thermodynamics
2. Derive some useful thermodynamic relation from the combined first and second laws.

7.0 REFERENCES/FURTHER READING

- Adams, S. & Allday, J. (2000). *Advanced Physics*. Oxford University Press, UK.
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UNIT 2 THERMODYNAMIC POTENTIALS

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1.0 INTRODUCTION

Energy functions of thermodynamic systems, also known as thermodynamic potentials, are discussed in this unit. They are useful in explaining many of the physical processes in thermodynamics

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- name all the thermodynamics potentials;
- define each of the thermodynamic potentials;
- derive differential forms of the thermodynamic potentials; and
- mention process that each of these thermodynamic potentials can be used to describe.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Thermodynamic Potentials

The four (4) thermodynamic potentials are;

- internal energy **U**
- enthalpy **H**
- helmholtz free energy **A**
- gibbs free energy **G**.

Depending on the thermodynamic constraints on a system, it is always convenient to use a particular thermodynamic potential to describe a system. For example, Helmholtz free energy **A** can be used to describe a system in which temperature and volume are held constant. The equilibrium condition for this system is $dA=0$. Gibbs free energy **G** can be used to describe equilibrium between phases (since the two phases share the same pressure and temperature).

3.2 Internal Energy U

The internal energy **U** of a system is a state function i.e. it depends on the state of a system. The first law of thermodynamics (Module 2, unit 1) gives an insight into the internal energy of a system. Change in internal energy **U** of a system ΔU , according to the first law of thermodynamics is

$$\Delta U = Q - W$$

And the differential form is

$$dU = dQ - dW \quad 11.1$$

The work done on a system may comprise of an irreversible component dW_I (such as stirring with a paddle, or forcing an electric current through a resistor) and some reversible components dW_R . The irreversible component of work is dissipated as heat and is identical to adding heat to the system. So we can write $dS = \frac{dQ + dW_I}{T}$ and this gives $dQ = TdS - dW_I$. The reversible component of the work may consist of work done in compressing the system (PdV), but there may also be other kinds of work, such as the ones listed in section 3.1.1 in module 2, unit 1. In general the expression for each of these forms of reversible work is of the form XdY , where X is an intensive state variable and Y is an extensive state variable. All of these forms of non-dissipative work can collectively be called configuration work.

Therefore, the total work done on the system is of the form

$$dW = dW_I - PdV + \sum XdY \quad 11.2$$

so, the first law of thermodynamics takes the form

$$dU = dQ + dW_I - PdV + \sum XdY \quad 11.3$$

Equation 11.3 is a sort of ‘complete form’ of the first law taking into consideration all possible forms of work. Using equation 11.3, if a particular system is held at constant volume, then no PdV work of expansion or compression is done. And if no other sort of work is done (either non- PdV reversible work or irreversible work dW_I), then the increase in internal energy of this system is just equal to the heat added to the system.

Therefore, internal energy U can be used to describe a system in which heat is transferred (either in or out) and / or work is done on or by the system.

3.2 Internal Energy U

The internal energy U of a system is a state function i.e. it depends on the state of a system. The first law of thermodynamics (Module 2, unit 1) gives an insight into the internal energy of a system. Change in internal energy U of a system ΔU , according to the first law of thermodynamics is

$$\Delta U = Q - W$$

And the differential form is

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so, the first law of thermodynamics takes the form

$$dU = dQ + dW_I - PdV + \sum XdY \quad 11.3$$

Equation 11.3 is a sort of ‘complete form’ of the first law taking into consideration all possible forms of work. Using equation 11.3, if a particular system is held at constant volume, then no PdV work of expansion or compression is done. And if no other sort of work is done (either non- PdV reversible work or irreversible work dW_I), then the increase in internal energy of this system is just equal to the heat added to the system.

Therefore, internal energy U can be used to describe a system in which heat is transferred (either in or out) and / or work is done on or by the system.

3.4 Helmholtz Free Energy A

The Helmholtz free energy A is defined as

$$A = U - TS \quad 11.7$$

Its differential form is

$$dA = dU - TdS - SdT \quad 11.8$$

But $dU = dQ + dW_I - PdV + \sum XdY$, so equation 11.8 becomes

$$dA = -SdT - PdV + \sum XdY \quad 11.9$$

Equation 11.9 tells us that in an isothermal process (i.e when $dT = 0$), the increase in the

Helmholtz function of a system is equal to all the reversible work ($-PdV + \sum XdY$) done on the system. On the other hand, if a machine does any reversible work at constant temperature, the Helmholtz function decreases, and the decrease in the Helmholtz function is equal (if temperature is constant) to the reversible work (of all types) done by the system.

3.5 Gibbs Free Energy G

The Gibbs function is define as

$$G = U - TS + PV \quad 11.10$$

It can also be defined as

$$G = H - TS \quad 11.11$$

and as

$$G = A + PV \quad 11.12$$

Its differential from equation 11.11 is

$$dG = dH - TdS - SdT, \quad 11.13$$

and from 11.12 is

$$dG = dA + PdV + VdP \quad 11.14$$

But from equation 11.6 ($dH = TdS + VdP + \sum XdY$) or from equation 11.9 ($dA = -SdT - PdV + \sum XdY$) equation 11.13 or 11.14 becomes

$$dG = -SdT + VdP + \sum XdY \quad 11.15$$

Equation 11.15 can be used to describe a system that undergoes constant temperature and constant pressure processes. Example of a process of this kind is the phase change of a pure substance that usually takes place at constant temperature and pressure. Hence, the Gibbs free function is very useful in describing a process that involves change of phase.

3.6 Differential Form of Thermodynamic Potential

The differential forms of the thermodynamic potentials are:

$$dU = dQ + dW_I - PdV + \sum XdY \quad 11.16$$

$$dH = TdS + VdP + \sum XdY \quad 11.17$$

$$dA = -SdT - PdV + \sum XdY \quad 11.18$$

$$dG = -SdT + VdP + \sum XdY \quad 11.19$$

The more familiar forms of thermodynamic potentials are:

$$dU = TdS - PdV \quad 11.20$$

$$dH = TdS + VdP \quad 11.21$$

$$dA = -SdT - PdV \quad 11.22$$

$$dG = -SdT + VdP \quad 11.23$$

Equations 11.20 to 11.23 are for condition under which only reversible work done on or by a system is PdV work of expansion or of compression.

SELF ASSESSMENT EXERCISE 1

- i. Define each of the four thermodynamic potentials
- ii. Derive the differential forms of the four thermodynamic potentials

4.0 CONCLUSION

Thermodynamics potentials are treated in the unit. Emphasis was on their definition, their differential forms, and their usefulness. Besides using these thermodynamic potentials in describing thermodynamic processes, useful relations can also be derived from each of these thermodynamic potentials. This will be the focus of the next unit.

5.0 SUMMARY

In this unit you have learnt that:

- there are four (4) thermodynamic potentials are namely; entropy **U**, enthalpy **H**, Helmholtz free energy **A** and Gibbs free energy **G**
- their differential forms can be obtained from their definitions
- depending on the constraints imposed on a system, it is always convenient to use a particular thermodynamic potential to describe a system.

6.0 TUTOR - MARKED ASSIGNMENT

1. List all the thermodynamic potentials
2. Define each of the thermodynamic potentials
3. Derive differential forms of thermodynamic potential
4. Describe the process that each of these thermodynamic potentials are involved with.

7.0 REFERENCES/FURTHER READING

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UNIT3 THE MAXWELL RELATIONS OF THERMODYNAMICS

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1.0 INTRODUCTION

Useful relations can be derived from each of the four thermodynamic potentials discussed in the last unit. These relations are called Maxwell's relations of thermodynamics. This unit therefore focuses on derivation of Maxwell's relations.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- derive each of the four Maxwell's relations from the differential of the thermodynamics potentials; and
- give the importance of these relations.

2.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 Definition

The differential forms of the thermodynamic potentials are:

$$dU = TdS - PdV \quad 12.1$$

$$dH = TdS + VdP \quad 12.2$$

$$dA = -SdT - PdV \quad 12.3$$

$$dG = -SdT + VdP \quad 12.4$$

The four Maxwell relations are derived from each of these four thermodynamic potentials.

3.2 1st Relation

The differential form of internal energy U is

$$dU = TdS - PdV$$

Differentiating this with respect to S while V is kept constant gives

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad 12.5a$$

and with respect to V while S is kept constant gives

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad 12.5b$$

Also differentiating 12.5a with respect to V at constant S and 12.5b with respect to S at constant V will give

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_S \quad 12.6a$$

and

$$\frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_V \quad 12.6b$$

The mixed second order derivatives of U , which implies that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 12.7$$

Equation 12.7 is one of the four Maxwell relations.

3.3 2nd Relation

From differential form of Enthalpy **H** (i.e. $dH = TdS + VdP$)

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad 12.8a$$

and

$$\left(\frac{\partial H}{\partial P}\right)_S = P \quad 12.8b$$

Second derivative gives

$$\frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial T}{\partial P}\right)_S \quad 12.9a$$

and

$$\frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial P}{\partial S}\right)_P \quad 12.9b$$

The mixed second order derivatives of **H** are equal, so

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial P}{\partial S}\right)_P \quad 12.10$$

Equation 12.10 is one of the four Maxwell's relations.

3.4 3rd Relation

From the differential of Helmholtz free energy **A** (i.e. $dA = -SdT - PdV$)

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad 12.11a$$

and

$$\left(\frac{\partial A}{\partial V}\right)_T = -P \quad 12.11b$$

Second derivative gives

$$\frac{\partial^2 A}{\partial V \partial T} = -\left(\frac{\partial S}{\partial V}\right)_T \quad 12.12a$$

and

$$\frac{\partial^2 A}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_V \quad 12.12b$$

The mixed second derivatives of **A** in equation 12.12 are equal, therefore

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

i.e.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad 12.13$$

$\left(\frac{\partial P}{\partial T}\right)_V$ in equation 12.13 can be obtained from equation of state. This implies that the variation of entropy **S** with respect to volume **V** at constant temperature **T** for a system can be obtained from equation of state for the system.

3.5 4th Relation

From differential of Gibb's free energy **G** (i.e. $dG = -SdT + VdP$), partial derivative gives

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad 12.14a$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad 12.14b$$

Differentiating 12.14a with respect to **P** at constant **T**, and 12.14b with respect to **T** at constant **P** give

$$\frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T, \quad 12.15a$$

and

$$\frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial V}{\partial T}\right)_P, \quad 12.15b$$

respectively.

The mixed second derivatives of **G** in equation 12.15 are equal, therefore

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 12.16$$

$\left(\frac{\partial V}{\partial T}\right)_P$ in equation 12.16 can be obtained from equation of state.

3.6 Maxwell Relations

The four (4) Maxwell Relations of thermodynamics are:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 12.17$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial P}{\partial S}\right)_P \quad 12.18$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad 12.19$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 12.20$$

3.7 Usefulness

These relations (i.e. Maxwell relations) are useful in thermodynamics calculations. For example, one can replace a derivative of entropy with a derivative of a simple thermodynamic variation such as temperature.

Equation 13 and 16 give the derivative of entropy in terms of temperature **T**, volume **V** and pressure **P**.

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

For an ideal gas, $PV = nRT$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} = \frac{P}{T} \quad 12.21$$

and

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} = \frac{V}{T} \quad 12.22$$

For an ideal gas, using equations 12.21 and 12.22, equations 12.13 and 12.20 respectively become

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{P}{T} \quad 12.23$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{V}{T} \quad 12.24$$

SELF ASSESSMENT EXERCISE

- i. Derive the four Maxwell equations.
- ii. For an ideal gas, show that $(\frac{\partial S}{\partial V})_T = \frac{P}{T}$ and $(\frac{\partial S}{\partial P})_T = -\frac{V}{T}$.
- iii. give the importance of these relation.

4.0 CONCLUSION

We have derived, in this unit, the four (4) Maxwell relations and we also mentioned the usefulness of these relations. In the next unit, we will be using these relations in deriving the TdS equations.

5.0 SUMMARY

In this unit, you have learnt that:

- each of the four Maxwell's relations is derived from each of the four thermodynamics potentials
- maxwell relations are useful in thermodynamics calculations e.g. a derivative of entropy can be replace with a simple thermodynamic variation such as temperature.

6.0 TUTOR-MARKED ASSIGNMENT

- i. For the differential of x given as

$$dx = M(y, z)dy + N(y, z)dz \text{ (equation 2.7)}$$

dx is exact when

$$\left(\frac{\partial M}{\partial z}\right)_y = \left(\frac{\partial N}{\partial y}\right)_z \text{ (equation 2.8)}$$

- ii. It is known that the differentials of the thermodynamic potentials are exact; hence derive the four Maxwell's relations using equations 2.7 and 2.8.

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UNIT 4 TDS EQUATIONS

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1.0 INTRODUCTION

Another useful set of equations in thermodynamics is the TdS equations. They, among other things, enable us to calculate the change in entropy during various reversible processes in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus.

2.0 A: OBJECTIVES

By the end of this unit, you should be able to:

- derive the three TdS equations
- write change in entropy for different reversible processes in term of directly measurable quantities.

3.0 B: HOW TO STUDY THIS UNIT

1. You are expected to read carefully through this unit twice before attempting to answer the activity questions. Do not look at the solution or guides provided at the end of the unit until you are satisfied that you have done your best to get all the answers.
2. Share your difficulties in understanding the unit with your mates, facilitators and by consulting other relevant materials or internet.
3. Ensure that you only check correct answers to the activities as a way of confirming what you have done.
4. Note that if you follow these instructions strictly, you will feel fulfilled at the end that you have achieved your aim and could stimulate you to do more.

3.0 MAIN CONTENT

3.1 First TdS Equation

Entropy (**S**) can be express in terms of any two of **P**, **V**, and **T**. Let us express entropy **S** as a function of **V** and **T**, i.e. **S** (**V**,**T**). The derivative of entropy **S** is

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT \quad 13.1$$

Multiply equation 13.1 by **T** to obtain

$$TdS = T\left(\frac{\partial S}{\partial V}\right)_T dV + T\left(\frac{\partial S}{\partial T}\right)_V dT \quad 13.2$$

From Maxwell's relation (i.e. 12.19), $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and also at constant volume $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V$, therefore 13.2 becomes

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT \quad 13.3$$

Equation 13.3 is the first TdS equation.

3.2 Second TdS

Let us express entropy **S** in terms **P** and **T** i.e. **S**(**P**,**T**), its derivative is

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \quad 13.4$$

Multiplying 13.4 by **T** gives

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_T dP + T\left(\frac{\partial S}{\partial T}\right)_P dT \quad 13.5$$

From Maxwell's relation (equation 12.20), $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, and also at constant pressure $T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = C_P$. Thus 13.5 becomes

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT \quad 13.6$$

Equation 13.6 is the second TdS equation

3.3 Third TdS

Then the last option is to express entropy S as a function of P and V , i.e. $S(P, V)$, we have

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV \quad 13.7$$

Multiplying 13.7 by T to obtain

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV \quad 13.8$$

In a constant volume process, it can be proved that $T\left(\frac{\partial S}{\partial P}\right)_V = C_V\left(\frac{\partial T}{\partial P}\right)_V$.

And also in a constant pressure process, it can be proved that $T\left(\frac{\partial S}{\partial V}\right)_P = C_P\left(\frac{\partial T}{\partial V}\right)_P$.

Therefore 13.8 becomes

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \quad 13.9$$

Equation 13.9 is the third of the **TdS** equations.

Therefore the three TdS equations are

$$TdS = T\left(\frac{\partial P}{\partial T}\right)_V dV + C_V dT \quad 13.10$$

$$TdS = -T\left(\frac{\partial V}{\partial T}\right)_P dP + C_P dT \quad 13.11$$

$$TdS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV \quad 13.12$$

These equations enable one to calculate heat flow (TdS) in a reversible process. Also, change in entropy between two states of a system can be calculated from these equations provided that the equations of state is known. This is because all the partial derivatives in these equations can be obtained from equation of state

3.4 Expansion, Compression and TdS Equations

3.4.1 Compression

The way the volume of a material decreases with pressure at constant temperature is described by isothermal compressibility k

$$k = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad 13.13$$

Isothermal compressibility is different from another parameter called adiabatic compressibility k_{ad} .

$$k_{ad} = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s \quad 13.14$$

The reciprocal of k (i.e. $\frac{1}{k}$) is called isothermal bulk modulus or isothermal incompressibility.

3.4.2 Expansion

The way the volume of a material increases with temperature at constant pressure is described by coefficient of volume expansion or expansivity β

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad 13.15$$

The unit of expansivity is K^{-1}

Using equations 13.13 and 13.15, one can show that

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k} \quad \text{and} \quad \left(\frac{\partial V}{\partial T} \right)_P = \beta V \quad 13.16$$

and the reciprocal of 13.16 gives

$$\left(\frac{\partial T}{\partial P} \right)_V = \frac{k}{\beta} \quad \text{and} \quad \left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{\beta V} \quad \text{respectively} \quad 13.17$$

SELF ASSESSMENT EXERCISE 1

- Using equation 13.13 and 13.15, show that $\left(\frac{\partial P}{\partial T} \right)_V = \frac{\beta}{k}$
- Determine the heat transferred during a reversible isothermal change in pressure.

- iii. Calculate the temperature change of a substance which undergoes a reversible adiabatic change of pressure.

3.5 The TdS equations in terms of k and β

Replacing the partial derivatives with these, the three TdS equations become

$$dS = \frac{\beta}{k} dV + \frac{C_V}{T} dT \quad 13.18$$

$$dS = -\beta V dP + \frac{C_P}{T} dT \quad 13.19$$

$$dS = \frac{C_V k}{T\beta} dP + \frac{C_P}{T\beta V} dV \quad 13.20$$

Equations 13.18 to 13.20 give the change in entropy between two states in terms of P , V , T , k , β and heat capacities as a function of temperature and pressure of specific volume. The implication of these equations is that one doesn't even need equation of state to calculate the change in entropy.

4.0 CONCLUSION

The three TdS equations are useful set of equation in thermodynamics. They are used to calculate heat flow in any reversible process.

5.0 SUMMARY

In this unit, you have learnt:

- how to derive the three TdS equations
- that these equations can be used to calculate heat flow (TdS) in a reversible process.

6.0 TUTOR-MARKED ASSIGNMENT

1. Using the TdS equations 13.18 and 13.19 show that $C_P - C_V = \frac{TV\beta^2}{\kappa}$.
2. Write change in entropy for different reversible process in terms of directly measurable qualities

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