4. THERMODYNAMICS

Learning outcomes

After the lesson, learners should be able to:

- ✓ Define thermodynamics.
- ✓ Define system, surrounding, boundary, and universe
- ✓ Define closed, open, and isolated systems
- ✓ Explain the energy change in chemical reactions.
- ✓ Define the terms internal energy and state function. (enthalpy of solution, enthalpy of formation, enthalpy of combustion, and enthalpy of reaction).
- ✓ State and explain the first law of thermodynamics.
- ✓ State and explain enthalpy and enthalpy changes in various processes
- ✓ Explain endothermic and exothermic processes with the help of an energy profile diagram.
- ✓ State laws of thermochemistry and solve numerical problems related to the Hess law.
- ✓ Define the term entropy and spontaneity.
- ✓ State and explain the second law of thermodynamics.
- ✓ Define standard Gibbs free energy change of reaction by means of the equation $\Delta G = \Delta H - T\Delta S$.
- ✓ Calculate ΔG for a reaction using the equation $\Delta G = DH - TDS$.
- ✓ State whether a reaction or process will be spontaneous by using the sign of ΔG.
- ✓ Explain the relationship between ΔG and the equilibrium constant.

Introduction

1. What is thermodynamics? 1

1. Study of flow of heat or any other forms of energy into or out of the system of physical and chemical change is
    a. Thermochemistry c. thermodynamics
    b. Thermokinetics d. thermochemical study

- **System (Homogeneous and heterogeneous systems)**
- **Surrounding**
- **Boundary**
- **Open/Close and isolated systems**

2. An isolated system is a system in which
    a. There is no change of energy with the surroundings.
    b. There is an exchange of mass and energy with the surroundings.
    c. There is no exchange of mass and energy with the surroundings.
    d. There is an exchange of mass with the surroundings.
3. A well-stoppered thermos flask contains some ice cubes. This is an example of
    a. Closed system
    b. Open system
    c. Isolated system
    d. Non-thermodynamic system

- **System of states and state functions**

  T, P, V, n, E, H, S, G, etc. vs *q, w, etc.*

2. What is meant by state function? Give its example. 2

4. Which of the following is not a state function?
    a) Temperature b) entropy c) enthalpy d) work

- **Extensive and intensive properties**

  V, n, wt. E, H, S, G molar volume, T, d, sp gr, B. Pt., etc.

5. Which of the following thermodynamic variables is extensive?
   a) Pressure b) density c) temperature d) mass
6. Which of the following is an intensive property?
   a) Volume b) internal energy c) entropy d) mass/volume
7. An example of extensive property is
   a. enthalpy b. internal energy
   c. both a and b d. none

7. Identify the intensive quantity from the following
   a. enthalpy and temperature b. volume and temperature
   c. enthalpy and volume d. temperature and refractive index

3. Distinguish between intensive and extensive property with examples. 2
4. State whether the following properties are extensive properties or intensive properties. A) Entropy B) Temperature 2

Energy in chemical reactions

Heat

Work done
Work = pressure x volume

Sign conventions
Heat gained by the system = + ve
Heat lost by the system = -ve

Work done on the system = +ve
Work done by the system = -ve
1 calorie = 4.184 joule

8. ΔH for the combustion of a compound is
   a) Positive b) negative c) zero d) may be +ve or -ve

Internal Energy

Features
Extensive
Absolute values cannot be determined
State function- change can be determined.
$\Delta E = E_2 - E_1$

5. Define the term internal energy. 1

9. Internal energy does not include
   a. Vibrational energy c. rotational energy
   b. Gravitational energy d. nuclear energy

The first law of Thermodynamics

Total energy of the system and surroundings remains constant
Energy can neither be created nor destroyed by one form of energy may change into another form.
It is impossible to construct a perpetual motion machine which can produce work without spending energy on it.
Formulation of the first law

Different forms

1. **Isobaric**
2. **Isothermal**
3. **Isochoric**
4. **Adiabatic**

6. State the first law of thermodynamics and write its mathematical relation. 2
7. State the first law of thermodynamics. What are its advantages and limitations? 2
8. State the first law of thermodynamics and point out its limitations.
9. State and explain the first law of thermodynamics, and, hence, deduce H=E+PV, where all the symbols have usual meanings. 5

10. Prove that (i) $\Delta E = Qv$ at constant volume and (ii) $\Delta H = Qp$ at constant pressure 1+1

10. A system absorbs 10 kJ of heat and does 6 kJ of work, the internal energy of the system
    a. Decreases by 4 kJ
    b. Increases by 14 kJ
    c. increases by 4 kJ
    d. decreases by 14 kJ

Enthalpy and enthalpy change in chemical reactions

A standard enthalpy change refers to the energy transferred at 298 K and standard pressure (usually 1 atmosphere or 101 kPa).

H = E + PV

11. Distinguish between internal energy and enthalpy. 2

Energy profile diagrams

Any chemical reaction will involve breaking some bonds and making new ones. Energy is needed to break bonds and is given out when new bonds are formed. It is improbable that these two processes will involve exactly the same amount of energy, and so some energy will either be absorbed or released during a reaction.

Usually, the energy changes involve heat, but they can also involve sound, light or even electrical energy.
Reactions that **give out heat** are called exothermic reactions.
Reactions that **take in energy** are known as endothermic reactions.
Enthalpy change, ΔH: the heat energy transferred during a chemical reaction
For an exothermic reaction, heat is lost from the reactants. The value of ΔH is negative.
For an endothermic reaction, heat is gained by the reactants. The value of ΔH is positive.
Enthalpy changes are measured in kJ mol^{-1}.

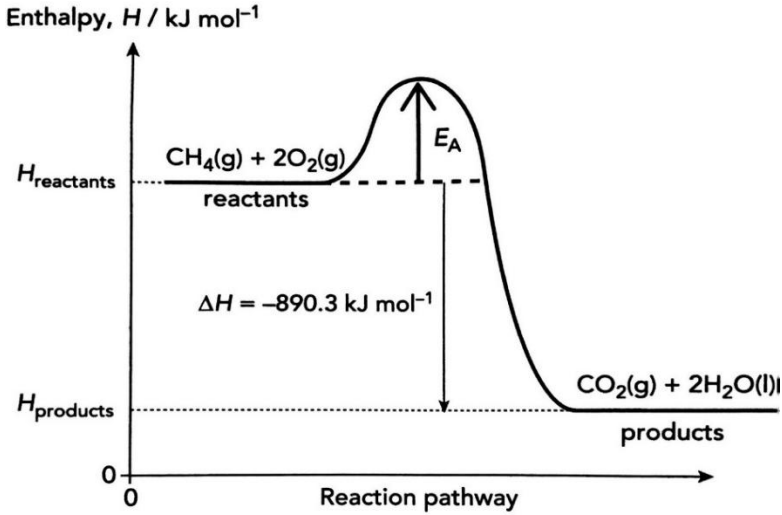


Figure: Energy change in an exothermic reaction

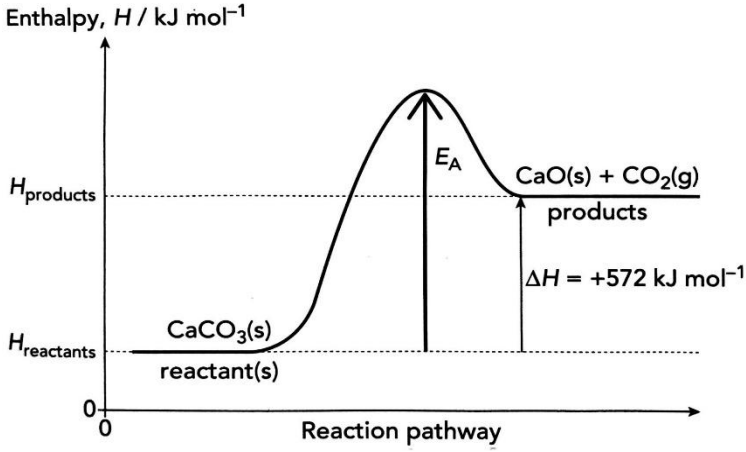


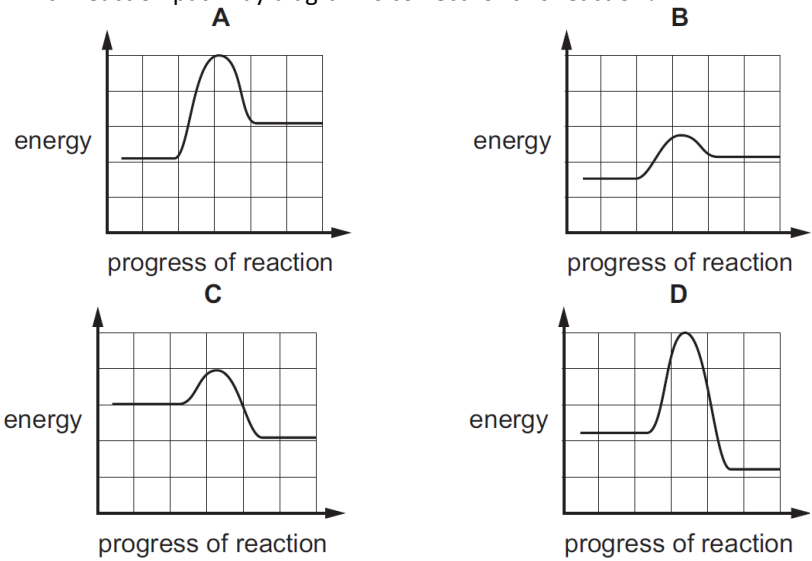
Figure: Energy change in an endothermic reaction

Activation energy, E_A: the minimum energy the colliding particles must possess to break bonds to start a chemical reaction.

12. Define exothermic and endothermic reactions. 2
13. Draw the energy profile diagram for exothermic and endothermic reactions. 2
14. Distinguish between exothermic and endothermic reactions. 2

15. Draw an energy profile diagram showing the energy of activation for an endothermic reaction. 2

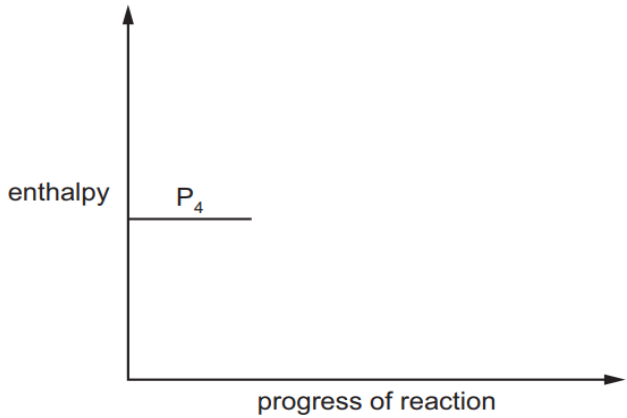
11. The enthalpy change of reaction $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3\ (g)$ is -93.7 kJ. Then the above reaction is
    a. Exothermic
    b. Isothermal
    c. endothermic
    d. reversible
12. For a certain endothermic reaction, the activation energy is numerically equal to twice the enthalpy change of reaction.
    Which reaction pathway diagram is correct for this reaction?



16. Red phosphorus (P) forms when white phosphorus (P_4) is exposed to sunlight.

$$\underset{\text{white}}{\tfrac{1}{4}P_4(s)} \rightarrow \underset{\text{red}}{P(s)} \qquad \Delta H = -17.6\,\text{kJ mol}^{-1}$$

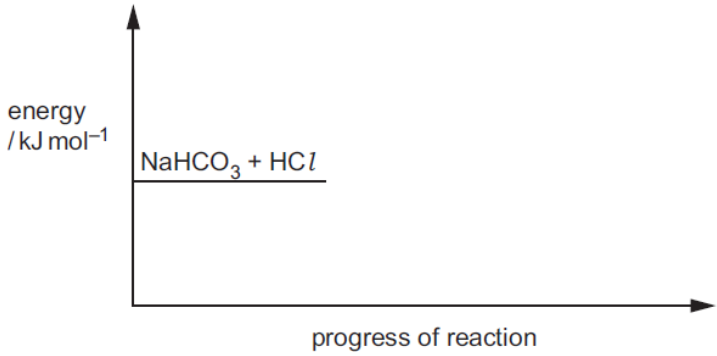
Use this information to draw a reaction pathway diagram to show the formation of red phosphorus (P) from white phosphorus (P_4).



17. Separate samples of Na_2CO_3 and $NaHCO_3$ react with HCl (aq) to produce the same products, as shown in Table

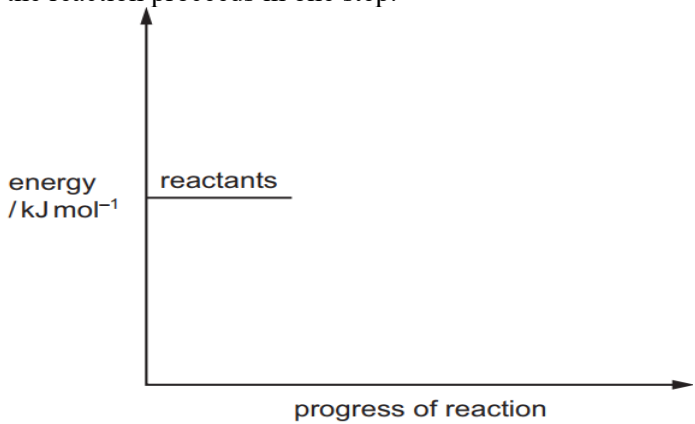
reaction	equation	ΔH/kJ mol^{-1}
1	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$	ΔH_1
2	$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$	$\Delta H_2 = +27.2$

Complete the reaction pathway diagram in Fig. 2.1 for reaction 2.
Label the diagram to show the enthalpy change, ΔH_2, and the activation energy, E_A.

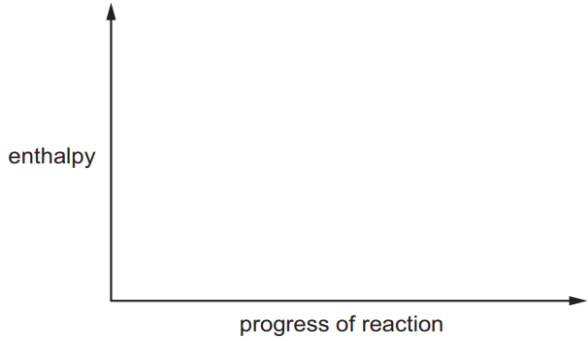


18. Krypton reacts with fluorine in the presence of ultraviolet light to make krypton difluoride, $KrF_2(g)$.
$Kr(g) + F_2(g) \rightarrow KrF_2(g)$
activation energy for the reaction, $E_a = +385 kJmol^{-1}$
enthalpy change of formation of KrF_2, $\Delta H_f = +60.2 kJmol^{-1}$
(i) Use this information to complete the reaction profile diagram for the

formation of KrF_2.
Label E_a and ΔH_f on the diagram.
Assume the reaction proceeds in one step. [2]



19. Magnesium, Mg, burns in oxygen, O_2.
The activation energy, E_a, for this reaction is $+148 kJmol^{-1}$.
On the following figure:
● sketch a reaction pathway diagram for the reaction that occurs when Mg burns in O_2
● label the diagram to show the enthalpy change, ΔH, and the activation energy, E_a, for the reaction.



13. The enthalpy changes for the possible reactions W, X, Y and Z are given.
W $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $\Delta H^o = -56 kJ\ mol^{-1}$
X $NaCl(aq) + H_2O(l) \rightarrow NaOH(aq) + HCl(aq)$ $\Delta H^o = +56 kJ\ mol^{-1}$
Y $2HI(g) \rightarrow H_2(g) + I_2(g)$ $\Delta H^o = +11 kJ\ mol^{-1}$
Z $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\Delta H^o = -11 kJ\ mol^{-1}$

Which statement about the activation energies of these reactions is correct?

A X is greater than W; Z is greater than Y.

B X is greater than W; Y is greater than Z.

C W is greater than X; Z is greater than Y.

D W is greater than X; Y is greater than Z.

14. An endothermic reaction is one in which
    a. Heat is liberated
    b. Heat is absorbed
    c. Temperature remains constant
    d. Heat is liberated if done at constant
15. An exothermic reaction is one in which the reacting substances
    a. Have more energy than the products.
    b. Have less energy than the products.
    c. Have the same energy as the products.
    d. Are at a higher temperature.
16. Which of the following statements is false for the change

    $H_2(g) \rightarrow 2H(g) \quad \Delta H = +104$ Kcal

    a. The reaction is endothermic.
    b. 2.0 g of H(g) contains more energy than 2.0 g of $H_2(g)$.
    c. 2.0 g of $H_2(g)$ contains more energy than 2.0 g of H(g).
    d. Heat is absorbed in the reaction.

Enthalpy of reaction

The standard enthalpy change of reaction **is the enthalpy change when the amounts of reactants shown in the stoichiometric equation react to give products under standard conditions. The reactants and products must be in their standard states.**

20. What is the enthalpy of reaction? 1

17. The equation for a chemical reaction is shown. All substances are in their standard states.

    $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$

    Which statement describes the standard enthalpy change of reaction for this reaction?

    A the enthalpy change when a total of one mole of products is produced

    B the enthalpy change when a total of one mole of reactants is reacted

C the enthalpy change when one mole of water reacts
D the enthalpy change when six moles of hydrogen fluoride are produced

Enthalpy of formation ΔH_f

The standard enthalpy change of formation, is the enthalpy change **when one mole of a compound is formed from its elements** under standard conditions. The reactants and products must be in their standard states.
By definition, the standard enthalpy change of formation of any element in its standard state is zero.

21. Define standard enthalpy of formation. 1
22. Define heat of formation. 1

18. Which equation has an enthalpy change equal to the standard enthalpy of formation of sodium oxide?
A $Na(s) + 1/4\, O_2(g) \rightarrow {}_{1/2}\, Na_2O(s)$
B $Na(s) + O_2(g) \rightarrow Na_2O(s)$
C $2Na(s) + {}_{1/2}\, O_2(g) \rightarrow Na_2O(s)$
D $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$
19. For which equation is the enthalpy change correctly described as an enthalpy change of formation?
A $C(g) + O_2(g) \rightarrow CO_2(g)$
B $C(s) + ½\, O_2(g) \rightarrow CO(g)$
C $2N(g) + 4O(g) \rightarrow N_2O_4(g)$
D $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
20. For which equation is the enthalpy change correctly described as an enthalpy change of formation?
A $2NO(g) \rightarrow N_2(g) + O_2(g)$
B $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
C $H_2O(l) + NaCl(s) \rightarrow NaCl(aq)$
D $K(s) + Mn(s) + 2O_2(g) \rightarrow KMnO_4(s)$
21. Which equation represents the reaction whose standard enthalpy change is the standard enthalpy change of formation of water?
A $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$
B $H_2(g) + ½\, O_2(g) \longrightarrow H_2O(l)$

C $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

D $2H(g) + O(g) \longrightarrow H_2O(l)$

22. Which reaction has an enthalpy change equal to the standard enthalpy change of formation of propane?

A $3C(g) + 4H_2(g) \rightarrow C_3H_8(g)$

B $3C(g) + 8H(g) \rightarrow C_3H_8(g)$

C $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$

D $3C(s) + 4H_2(g) \rightarrow C_3H_8(l)$

23. Skiers trapped by snowstorms use heat packs to keep warm. The heat may be generated by the reaction below.

$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$; $\Delta H = -1648$ kJ

What is the standard enthalpy change of formation of iron(III) oxide?

A 0 kJ mol^{-1} **B** –824 kJ mol^{-1} **C** –1648 kJ mol^{-1} **D** –3296 kJ mol^{-1}

Enthalpy of combustion ΔH_c

The standard enthalpy change of combustion is the enthalpy change **when one mole of a substance is burnt in excess oxygen** under standard conditions. The reactants and products must be in their standard states.

23. Define enthalpy of combustion. 1
24. Define heat of combustion. 1
25. Distinguish between enthalpy of combustion and enthalpy of formation. 2

24. Given that: ½ $S_8(g) + 6\ O_2 \longrightarrow 4\ SO_3(g)$, $\Delta H = -1590$ KJ:

The enthalpy of combustion of sulphur is

a. -1590 KJ mol^{-1} c. -3180 KJ mol^{-1}

b. +1590 KJ mol^{-1} d. -795 KJ mol^{-1}

25. The equation for a reaction is shown.

$H_2(g) + O_2(g) \rightarrow H_2O(l)$; $\Delta H = x$ kJ mol^{-1}

Which pair of descriptions is fully correct for this reaction?

	type(s) of enthalpy change	value of *x*
A	formation only	Positive
B	formation only	Negative
C	combustion, formation	Positive
D	combustion, formation	Negative

26. The heat of reaction in the following chemical reaction $H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ is termed as
    a. Enthalpy of formation
    b. Enthalpy of reaction
    c. Enthalpy of combustion
    d. Enthalpy of solution
27. Heat of combustion is always
    a. +ve b. -ve c. 0 d. indefinite quantity

Enthalpy of neutralization

ΔHneut

The standard enthalpy change of neutralisation **is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.**

26. What is the enthalpy of neutralization? Explain why the enthalpy of neutralization of a strong acid and a strong base is always a constant value. Why for the reaction of a weak acid and a strong base and vice versa it is different? 3

28. What is the definition of the enthalpy change of neutralization $\Delta H^{\ominus}_{\text{neut}}$?

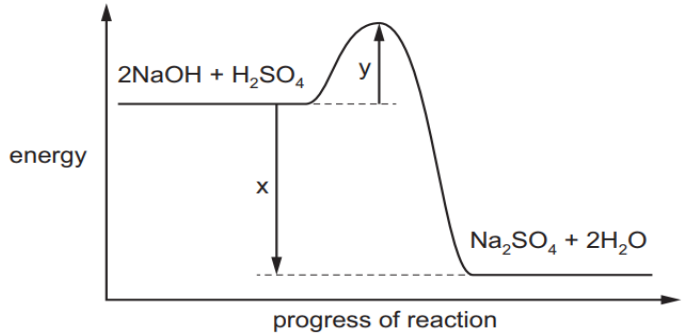
A $\Delta H^{\ominus}_{\text{r}}$ when one mole of an aqueous acid is neutralised by an aqueous alkali.

B $\Delta H^{\ominus}_{\text{r}}$ when one mole of an aqueous alkali is neutralised by an aqueous acid.

C $\Delta H^{\ominus}_{\text{r}}$ when one mole of an aqueous acid is neutralised by one mole of an aqueous alkali.

D $\Delta H^{\ominus}_{\text{r}}$ when an aqueous acid and an aqueous alkali react together to produce one mole of water.

29. A reaction pathway diagram for the reaction of aqueous sodium hydroxide and dilute sulfuric acid is shown.



What is the value of the enthalpy change of neutralisation, ΔH_{neut}?

A x B x – y C x/2 D (x-y)/2

30. Identify each of the following reactions as $\Delta H_f^{\ominus}$, $\Delta H_c^{\ominus}$ or $\Delta H_r^{\ominus}$

$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

$C(graphite) + O_2(g) \rightarrow CO_2(g)$

$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$

31. Which statement about enthalpy changes is correct?

A Enthalpy changes of reaction are always negative.

B Enthalpy changes of combustion are always positive.

C Enthalpy changes of formation are always positive.

D Enthalpy changes of neutralisation are always negative.

32. Which of the following statement is correct?

A ΔH is positive for endothermic reactions.

B ΔH is negative for endothermic reactions.

C The heat of neutralization of a strong acid and a strong base is always the same.

D the enthalpy of fusion is $-\Delta H$

33. What is the enthalpy change in the following reaction, $2CO + O_2 \rightarrow 2\ CO_2$ called?

a. Enthalpy of combustion
b. Enthalpy of fusion
c. enthalpy or formation
d. enthalpy of reaction

Laplace law

27. When 1 g of liquid naphthalene ($C_{10}H_8$) solidifies, 149 J of heat is evolved. Calculate the heat of fusion of naphthalene. 2

Hess' law of constant heat summation

The first law of thermodynamics also applies to chemical reactions: the total energy of the chemicals and their surroundings must remain constant. In 1840, Germain Hess applied the law of conservation of energy to enthalpy changes.

Hess's law: 'The enthalpy change accompanying a chemical change is independent of the route by which the chemical change occurs.'

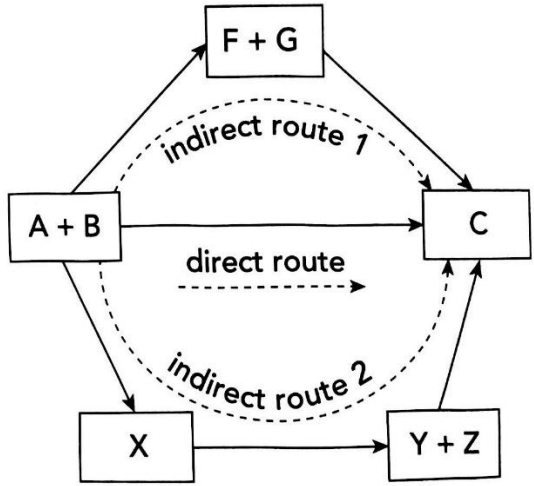


Fig: An enthalpy cycle (Energy cycle) or Hess cycle

28. State the Hess law of constant heat summation. 1
29. What is the Hess law of constant heat summation? 1
30. State and explain the Hess law of constant heat summation. 5
31. Write a short note on Hess's law of constant heat summation. 5
32. Write a short note on Hess's law of constant heat summation and its application. 5
33. Write any two applications of Hess's law. 1
34. Mention the important applications of Hess's law of constant heat summation. 1
35. Hess' law is applied to calculate the different types of enthalpy of reactions.
    i) Define the Hess law of constant heat summation.

ii) What is meant by the enthalpy of reaction?

34. According to Hess's law, the change in enthalpy in the chemical reaction depends on the
    a. Intermediate state
    b. Initial and final state
    c. initial state
    d. final state
35. The enthalpies of elements in their standard state are taken as zero. Hence the enthalpy of formation of a compound
    a. Should always be negative
    b. Should always be positive
    c. Will be equal to twice the energy of combustion
    d. May be positive or negative

Numericals

36. If the heat change for the following reaction is -1648kJ, what is the standard enthalpy of formation of Fe_2O_3

    $4\ Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$ (Ans:-824kj) 1

37. If the standard enthalpy formation of ammonia is -46kj mol^{-1}, what is the enthalpy of the following reaction?

    $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ (Ans: -92kj)1

38. Calculate the standard enthalpy of formation of water in the following reaction:

    $2\ H_2(g) + O_2 \longrightarrow 2\ H_2O(l),\ \Delta H = -136$ Kcal 1

39. The enthalpy of reaction for

    $N_2(g) + 3\ H_2(g) \longrightarrow 2NH_3(g)$ is -92.4kj.
    Calculate the enthalpy of formation of ammonia. 2

40. Calculate the enthalpy of formation of NH_3 from the following equation.

    $N_2(g) + 3\ H_2(g) \longrightarrow 2\ NH_3(g)$ H=-186kj(Ans:-93kj) 2

41. Enthalpy of formation of $H_2O(l)$, $CO_2(g)$ and $C_3H_7OH(l)$ are -286 $kJmol^{-1}$, -295 $kJmol^{-1}$ -210 $kJmol^{-1}$ respectively.
    i. What is meant by the enthalpy of formation? 1
    ii. Write down balanced thermochemical reactions for each of the above processes. 1
    iii. Calculate the enthalpy of combustion of $C_3H_7OH(l)$ from the above data. (Ans = -316 kJ/mol) 3

42. Standard enthalpies of formation of $H_2O_2(l)$ and $H_2O(l)$ are 188 kJ/mol and 286 kJ/mol, respectively. What will be the enthalpy change of the following reaction:
$2\ H_2O_2\ (l) \rightarrow 2\ H_2O(l) + O_2(l)$ **3**

43. If heat of formation of CO_2, H_2O and $C_6H_{12}O_6$ are -365 $kJmol^{-1}$, -269 $kJmol^{-1}$ and -1169$kLmol^{-1}$ respectively. Calculate the heat of combustion of glucose ($C_6H_{12}O_6$). 4
44. The enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and $CH_4(g)$ are -393.5, -286.2 and -74.8$kJmol^{-1}$ respectively. Calculate the enthalpy of combustion of methane. (-891.1) 3
45. The heat of combustion of methane, carbon, and hydrogen are -210Kcal, -94 Kcal, and -68 kCal respectively. Calculate the heat of formation of methane. (ans = -20kcal) 4
46. The heats of formation of ethyl alcohol, water, and carbon dioxide are -64.1kCal, -68.5kCal, and -95kCal. Calculate the heat of combustion of ethyl alcohol. (ans = -331.4 kcal) 4
47. Calculate the enthalpy of formation of benzene, if the enthalpy of combustion of benzene and carbon are -3280kJ/mol and -395kJ/mol, respectively. The enthalpy of formation of water is
-285kJ/mol. (ans = 55 kJ/mol) **5**

48. Enthalpy of formation of benzene is 55kJ/mol, enthalpy of formation of water and carbon dioxide are -285kJ/mol and -395kJ/mol, respectively. Calculate the enthalpy of combustion of benzene. (-3280 $kJmol^{-1}$) 4
49. The standard enthalpy of formation of $H_2O(l)$, $CO_2(g)$ and $C_6H_6(l)$ are -286, -393.5 and +49.02kJ mol^{-1} respectively at 298K. Calculate the standard enthalpy of combustion of $C_6H_6(l)$ at the given temperature. (ans = -3268.02 kJ mol^{-1}) 5
50. Calculate the enthalpy of formation of ethane at 298K, if the enthalpies of combustion of C, H, and C_2H_6 are -94.14, -68.47, and -373.3 kCal, respectively. (ans = -20.39) 5
51. The standard heat of formation of $SO_2(g)$ and $SO_3(g)$ are -296.6 kJ and -396kJ respectively. Calculate the H for the following reaction:
$SO_2(g) + 1/2O_2(g) \longrightarrow SO_3(g)$ **4**

52. Calculate the heat of formation of $CS_2(l)$ from the following data.
$C(s) + O_2(g) \rightarrow CO_2(g)$, $\Delta H = -395kJ$
$S(s) + O_2(g) \rightarrow SO_2(g)$, $\Delta H = -295kJ$
$CS_2(s) + 3O_2(g) \rightarrow CO_2(g) + SO_2(g)$, $\Delta H = -1110kJ$

(ans =215kJ)

53. Calculate the heat of formation of ethanol from the following data

$H_2(g) + ½\ O_2(g) \longrightarrow H_2O(l)$, H= -286.2 kJ/mol

$C(s) + O_2(g) \longrightarrow CO_2(g)$, H=-393.2 kJ/mol

$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ ΔH = -1368kJ/mol

(ans = -277kJ/mol)

54. Calculate the heat of combustion of glucose from the following data: 4

$C(s) + O_2(g) \longrightarrow CO_2(g)$, H=-395kJ

$H_2(g) + ½\ O_2(g) \longrightarrow H_2O(l)$, H= -269kJ

$6\ C(s) + 6\ H_2(g) + 3\ O_2(g) \longrightarrow C_6H_{12}O_6(s)$, H=-1169kJ

55. Enthalpies of solution of $BaCl_2.2H_2O$ and $BaCl_2$ are 8.8 and -20.6 KJ/mol, respectively. Calculate the heat of hydration of $BaCl_2$ to $BaCl_2.2H_2O$. 2

56. Calculate the standard heat of formation of $CH_4(g)$ form the following information.

$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ ΔH= -890.3 kJ
$C(graphite) + O_2(g) \longrightarrow CO_2(g)$ ΔH=-393.5 kJ
$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ ΔH=-571.7 kJ **5**

1. **Calculate the enthalpy of formation of $AlCl_3(s)$. Given**

(i) $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$, ΔH = -185 kJ
(ii) $HCl(g) + aq \rightarrow HCl(aq)$, ΔH = -73.5 kJ
(iii) $AlCl_3(s) + aq \rightarrow AlCl_3(aq)$, ΔH = -323 kJ
(iv) $2\ Al(s) + 6\ HCl(aq) \rightarrow 2\ AlCl_3(aq) + 2\ H_2(g)$, ΔH = -1050 kJ **4**

57. Calculate the heat of formation of acetic acid from the following data
$C(s) + O_2(g) \rightarrow CO2(g)$ ΔH= -99 kcal/mol
$H2(g) + 1/2\ O2(g) \rightarrow H2O(l)$ ΔH= -68 kcal/mol
$CH3COOH + 2\ O2(g) \rightarrow 2CO2(g) + 2\ H2O(l)$ ΔH = -208 kcal/mol

2. **Calculate the enthalpy of formation of Ethane from the following data:** **3**

$C(s) + O_2(g) \rightarrow CO_2(g)$	$\Delta H°_1$ = -393.5 KJ/mol

$H2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	$\Delta H°_2$ = -285.8 KJ/mol
$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$	$\Delta H°_3$ = -1560 KJ/mol

58. Calculate the heat of formation of naphthalene from the following data: 3

a) $C(s) + O_2(g) \rightarrow CO_2(g)$ ΔH = -94.405 k cal.

b) $2H_2 + O_2(g) \rightarrow 2H_2O(1)$ ΔH = -68.3K cal

c) $C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(1)$ ΔH = -1231.6K cal.

59. Heat of combustion of carbon(s), sulphur(s) and carbon disulphide(l) are -395kJ/mol, -295 kJ/mol and -1110kJ/mol respectively. Calculate the heat of formation of $CS_2(l)$. (125kJ/mol) 4

60. Calculate the heat of formation of ethyl alcohol from the given data. 4

Heat of formation of ethyl alcohol	**-330 kcal**
Heat of formation of carbon dioxide	**-94 kcal**
Heat of formation of water	**-68.5 kcal**

36. The standard enthalpy of formation of $NO_2(g)$ is +33.2 kJ mol^{-1}. The standard enthalpy of formation of $N_2O_4(g)$ is +9.2 kJ mol^{-1}. What is the standard enthalpy change for the reaction

$2NO_2(g) \rightarrow N_2O_4(g)$?

A –57.2 kJ mol^{-1}
B –24.0 kJ mol^{-1}
C +42.4 kJ mol^{-1}
D +75.6 kJ mol^{-1}

37. Calciumcarbide, CaC_2, reacts with water, as shown. The data below the equations how, in $kJmol^{-1}$, the standard enthalpies of formation of the compounds involved.

$CaC_2(s) + H_2O(l) \rightarrow CaO(s) + 2H_2(g)$
–60 –286 –635 +228
What is the standard enthalpy change of the reaction shown?
A –753 kJ mol^{-1}
B –61 kJ mol^{-1}
C +61kJ mol^{-1}
D +753kJ mol^{-1}

38. Ethanol is increasingly being used as a fuel for cars.
The standard enthalpy change of formation of carbon dioxide is –393 kJ mol^{-1}.The standard enthalpy change of formation of water is –286 kJ mol^{-1}.

The standard enthalpy change of formation of ethanol is –277 kJ mol^{-1}. What is the standard enthalpy change of combustion of ethanol?

A –1921 kJ mol^{-1} **B**–1367 kJ mol^{-1}

C –956 kJ mol^{-1} **D** –402 kJ mol^{-1}

39. For the given reactions

$C + O_2 \rightarrow CO_2$, $\Delta H = - x$ KJmol^{-1}

$2CO + O_2 \rightarrow 2CO_2$, $\Delta H = - y$ KJmol^{-1}

The enthalpy of formation of CO becomes

a. 2y-x b. 2x-y c. (y-2x)/2 d. (x-2y)/2

40. Which expression gives the standard enthalpy change of combustion of methane?

A $\Delta H_f^\ominus(CH_4) + \Delta H_f^\ominus(CO_2) - 2\Delta H_f^\ominus(H_2O)$

B $\Delta H_f^\ominus(CO_2) + 2\Delta H_f^\ominus(H_2O) + \Delta H_f^\ominus(CH_4)$

C $\Delta H_f^\ominus(CH_4) + 2\Delta H_f^\ominus(H_2O) - \Delta H_f^\ominus(CO_2)$

D $\Delta H_f^\ominus(CO_2) + 2\Delta H_f^\ominus(H_2O) - \Delta H_f^\ominus(CH_4)$

41. The equation for an enthalpy change is shown. The enthalpy change is Q.

$$2C(s) + 3H_2(g) + 3.5O_2(g) \xrightarrow{Q} 2CO_2(g) + 3H_2O(l)$$

What is the correct expression to calculate Q?

A $2 \times \Delta H_c^\ominus [CO_2(g)] - 3 \times \Delta H_f^\ominus [H_2(g)]$

B $3 \times \Delta H_f^\ominus [H_2O(g)] + 2 \times \Delta H_c^\ominus [CO_2(g)]$

C $2 \times \Delta H_f^\ominus [CO_2(g)] - 3 \times \Delta H_f^\ominus [H_2(g)]$

D $3 \times \Delta H_f^\ominus [H_2O(l)] + 2 \times \Delta H_f^\ominus [CO_2(g)]$

61. Define bond enthalpy. 1

62. Estimate the enthalpy change of the reaction

$H_2(g) + Cl_2(g) \longrightarrow 2\ HCl(g)$

Given: bond energy of H-H = 435 kJ/mol

Bond energy of Cl-Cl = 243 kJ/mol

Bond energy of H-Cl = 430 kJ/mol **3**

63. Calculate the enthalpy change for the reaction

$H_2C{=}CH_2(g) + H_2(g) \rightarrow H_3C{-}CH_3(g)$ the bond energies of C-H, C-C, C=C and H-H are 99, 83, 147, 104 kcal/mol, respectively.

a. – 30 b. -149 c. -177 d. +66 e. 53 g. -34 h. +69 i. -83 j. +157 k. +5 l. +465 m. 134 n. +88 o.

64. Propane has the following structure $CH_3CH_2CH_3$. Calculate the enthalpy change $\Delta H°$ for the reaction.

$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(g)$ **3**

Given the average bond enthalpies for various bonds (KJ/mol):

C-C	C-H	O=O	C=O	O-H
347	414	498	741	464

a. -166 b. -1662 c. -1315 d. +4353 e. -1680 f. -3846 g. +561 h.

42. Ethane can react with fluorine to produce 1,2-difluoroethane, $C_2H_4F_2$.

$C_2H_6 + 2F_2 \rightarrow C_2H_4F_2 + 2HF\ \Delta H = -960\ kJ\ mol^{-1}$

bond	energy / kJ mol^{-1}
C–H	410
C–C	350
F–F	158
H–F	562

What is the bond energy of the C–F bond in 1,2-difluoroethane?

A 407 kJ mol^{-1} **B** 474 kJ mol^{-1} **C** 486 kJ mol^{-1} **D** 972 kJ mol^{-1}

65. What is meant by spontaneous process? Write an example of it. 2
66. Distinguish spontaneous and non-spontaneous processes, giving an example of each? 2

Second law of thermodynamics

67. Write a short note on the second law of thermodynamics. 5
68. State and explain the second law of thermodynamics. 5
69. State and explain the second law of thermodynamics in terms of entropy change. 3
70. State the second law of thermodynamics. How would you explain the law in the light of entropy change? 5
71. State and explain the second law of thermodynamics. How does free energy change depend on the equilibrium constant? 5
72. Define the thermodynamic efficiency of the heat engine. How is the second law of thermodynamics stated in light of this term? 2

43. The concept of entropy was introduced by
a) The first law of thermodynamics
b) The second law of thermodynamics
c) The third law of thermodynamics
d) None of the above

Entropy

44. For the equilibrium reaction: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
Which of the following conditions are correct?
a. $\Delta H = 0, \Delta S = 0$ c. $\Delta H > 0, \Delta S > 0$
b. $\Delta H < 0, \Delta S < 0$ d. $\Delta H > 0, \Delta S < 0$
45. When a solid melts, there is
a) An increase in enthalpy c) no change in enthalpy
b) A decrease in enthalpy d)
46. What will be the value of ΔS for the conversion of ice into water when they are in equilibrium? ($\Delta H = 6 kJmol^{-1}$)
a. 0.022 kJ K^{-1} mol^{-1} c. 0.027 kJ K^{-1} mol^{-1}
b. 0.025 kJ K^{-1} mol^{-1} d. 0.0219 kJ K^{-1} mol^{-1}
73. Give the physical meaning of entropy. Write its unit. 2
74. What is the physical concept of entropy? 2
75. What is meant by molar entropy? Write its unit. 1+1
76. What is entropy? State the effect of increased temperature on the entropy of a substance. 2
77. Gases have the highest absolute entropy among the three states of matter. Give a reason. 1
78. Predict the criteria of spontaneity in light of entropy change. 2
79. The latent heat of fusion of ice is 336 Jg^{-1}. Calculate the molar entropy of fusion of ice at its normal melting point. 2
80. The enthalpy of vaporization of liquid diethyl ether (C2H5)2O is 26 KJ/mol at its boiling point (35 °C). Calculate $\Delta S°$ for the conversion of:
i) Liquid to vapour ii) vapour to liquid **1**

Gibbs' Free Energy & Prediction of Spontaneity

47. Which name is associated with the relation $\Delta G = \Delta H - T\Delta S$?

a) Maxwell b) Gibbs' Helmholtz d) Boltzmann
b) Avogadro

48. What does a negative value of ΔG indicate about a reaction?
    a. It is endothermic.
    b. It is spontaneous.
    c. It is not spontaneous.
    d. The equilibrium has been reached.
49. For a process to be spontaneous
    a) ΔG must be -ve c) ΔG must be +ve
    b) ΔH must be -ve d) ΔH must be +ve
50. Which of the following pairs of chemical reactions is certain to result in a spontaneous reaction?
    a. Exothermic and increasing disorder
    b. Endothermic and increasing disorder
    c. Exothermic and decreasing disorder
    d. Endothermic and decreasing disorder
51. What is the correct set of parameters for a reaction to be spontaneous?
    a) ΔG = +ve; ΔS = +ve and E° = +ve
    b) ΔG = -ve; ΔS = +ve and E° = +ve
    c) ΔG = +ve; ΔS = -ve and E° = +ve
    d) ΔG = -ve; ΔS = -ve and E° = -ve
52. A chemical reaction will be spontaneous if it is accompanied by a decrease of
    a. Free energy of a system
    b. Entropy of system
    c. Enthalpy of the system
    d. Internal energy of the system
53. A reaction occurs spontaneously with
    a. Δ G is positive
    b. Δ G is positive, and Δ S is positive
    c. Δ H is positive and Δ S is negative
    d. Both Δ H and ΔS are positive and $\Delta H > T\Delta S$
54. The spontaneous change is one in which the system has
    a. An increase in internal energy
    b. Lowering in enthalpy
    c. Lowering in free energy
    d. No energy change

81. i. Derive the relation $\Delta G = \Delta H - T\Delta S$. 3

ii. Show the relation that the decrease in free energy of the system is equal to the useful work obtained at constant temperature and pressure. 2

82. Derive the Gibbs-Helmholtz equation.
83. Define the term standard free energy of a reaction. 2
84. Define free energy. Derive an expression to relate Gibbs' free energy change to work. 5
85. Define Gibbs' free energy. 1
86. Define Gibbs' free energy change. Write the mathematical relation to predict the spontaneity. 2
87. What is free energy change? How is it related to the enthalpy change? 2
88. How is the free energy change of a reaction related to the enthalpy change and entropy change? 2
89. Under what conditions the free energy change becomes zero?
90. Comment on the statement "The decrease of enthalpy is not the sole criterion for the feasibility of the process." 2
91. Calculate entropy change (ΔS) and free energy change (ΔG) for the conversion of ice into water at equilibrium conditions when enthalpy change (ΔH) is $10 kJmol^{-1}$. 2
92. Calculate S and G for conversion of ice into water when they are in equilibrium at 0 °C (H = 4 kj/mol) (ans $\Delta S = 0.0146$; $\Delta G = 0$) 2
93. *Distinguish spontaneous and non-spontaneous processes, giving an example of each. 2*
94. *What is meant by spontaneous process? Write an example of it. 2*
95. How would you predict the spontaneity of a system in terms of free-energy change? 2
96. How would you predict whether a reaction is spontaneous, non-spontaneous, and at equilibrium in terms of free energy change? 3
97. Discuss the criteria of spontaneity and non-spontaneity of a reaction on the basis of its energy change. 3
98. Write a short note on spontaneity in light of entropy change, enthalpy change, and free energy change. 5
99. Discuss the criteria of spontaneity, non-spontaneity, and equilibrium of exothermic and endothermic reactions on the basis of free energy and entropy change. 5
100. How would you predict the spontaneity using the relation?
101. $T\Delta S_{total} = -\Delta G$ 2
102. Mention the proper conditions of a chemical reaction to become spontaneous if its H and S are positive. 2

103. Under what conditions is the reaction expected to occuri) spontaneous
ii)non-spontaneous
104. In order for a reaction to occur spontaneously, what is the criterion? 2
105. Under what conditions, reactions occur spontaneously? 1
106. Name the two criteria that must be met for a process to be spontaneous, regardless of the temperature. 2
107. How is the feasibility of exothermic and endothermic reactions predicted in light of free energy change and entropy change?
108. Predict whether it is possible or not to reduce MgO using C at 298 K using the following equation: If not, at what temperature does the reaction become spontaneous?

$MgO(s) + C(s) \rightarrow Mg(s) + CO(g)$; $\Delta H^\circ_{rxn} = 491.18$ KJ/mol

& $\Delta S^\circ_{rxn} = 197.67$ J/K/mol 2

109. For the following reaction, the values for enthalpy change and entropy change at 500 K are as follows;

$Ag_2O(s) \rightarrow 2\,Ag(s) + 1/2O_2(g)$

$\Delta H_{rxn} = 30.56$ KJ/mol $\Delta S_{rxn} = 66$ J/K/mol

Find out whether the reaction is spontaneous at this temperature. If not, then at what temperature would it become spontaneous?

Relationship between ΔG and the equilibrium constant

55. The correct relationship between free energy and equilibrium constant K of a reaction is

a. $\Delta G^0 = RT\ln k$ b. $\Delta G^0 = -RT\ln k$ c. $\Delta G = -RT\ln k$ d. $\Delta G^0 = RT\ln k$

110. Study the following data for the thermodynamic process $H_2O(l) \rightarrow H_2O(s)$ at different temperatures and at 1 atmospheric pressure.

Condition	Temperature	Entropy change in J/Kmol	
		Entropy of system	Entropy of surroundings
1	-1^0C	-25.68	+25.72
2	0^0C	-26.55	+26.88
3	$+1^0$C	-27.62	+27.42

a. Calculate the total entropy of the universe at given condition 3. 1

b. Can we predict the spontaneity of the given reaction at 0 °C? 1

c. Calculate the equilibrium constant for the fusion of ice at 1 °C. What is the effect of temperature on the entropy change of the reaction? 2+1

111. Water gas is prepared by passing steam over red-hot coke as:

$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$; Given the following data

Substance	**ΔH_f° (KJ mol^{-1})**	**S° (JK^{-1} mol^{-1})**
C(s)	0	5.74
H_2O (g)	-241.8	188.71
H_2 (g)	0	130.52
CO (g)	-110.52	197.56

a. Calculate ΔH° and ΔS° of the reaction. 1+1

b. Calculate ΔG° and equilibrium constant (K) of the reaction at 1000°C. Given R = 8.314 $Jmol^{-1}K^{-1}$ 1+1

c. Find the temperature at which the reaction attains equilibrium. 1

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****