Topic 1 Thermodynamics

Objective Questions I (Only one correct option)

- An ideal gas is allowed to expand from 1 L to 10 L against a constant external pressure of 1 bar. The work done in kJ is (2019 Main, 12 April I)
 - (a) 9.0 (b) 10.0 (c) 0.9 (d) 2.0
- 2. The difference between H and U (H U), when the combustion of one mole of heptane (l) is carried out at a temperature T, is equal to (2019 Main, 10 April II)
 (a) 4 RT (b) 3 RT (c) 4 RT (d) 3 RT
- **3.** A process will be spontaneous at all temperature if

							(2019	Main	10 Ap	ril I)
(a)	H	0 and	S	0	(b)	H	0 and	S	0	
(c)	H	0 and	S	0	(d)	H	0 and	S	0	

- 4. During compression of a spring the work done is 10 kJ and 2 kJ escaped to the surroundings as heat. The change in internal energy, U (in kJ) is (2019 Main, 9 April II) (a) 8 (b) 12 (c) 12 (d) 8
- 5. Among the following the set of parameters that represents path functions, is (2019 Main, 9 April I) (A) q W (B) q (C) W (D) H TS (a) (A) and (D) (b) (A), (B) and (C) (c) (B), (C) and (D) (d) (B) and (C)
- 6. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28 \text{ JK}^{-1} \text{ mol}^{-1}$, calculate U and pV for this process. $(R = 8.0 \text{ JK}^{-1} \text{ mol}^{-1})$ (2019 Main, 8 April II)
 - (a) U = 2.8 kJ; (pV) = 0.8 kJ(b) U = 14 J; (pV) = 0.8 J
 - (c) U = 14 kJ; (pV) = 0.03(c) U = 14 kJ; (pV) = 4 kJ
 - (d) U = 14 kJ; (pV) = 18 kJ
- Which one of the following equations does not correctly represent the first law of thermodynamics for the given processes involving an ideal gas ? (Assume non-expansion work is zero) (2019 Main, 8 April I)

- (a) Cyclic process : q = W
- (b) Adiabatic process : U = W
- (c) Isochoric process : U q
- (d) Isothermal process : q = W
- **8.** For silver, $C_p(J K^{-1} \text{mol}^{-1})$ 23 0.01 T. If the temperature (T) of 3 moles of silver is raised from 300 K to 1000 K at 1 atm pressure, the value of H will be close to (2019 Main, 8 April I)

(a)	62 kJ	(b)	16 kJ
(c)	21 kJ	(d)	13 kJ

9. For a diatomic ideal gas in a closed system, which of the following plots does not correctly describe the relation between various thermodynamic quantities?

(2019 Main, 12 Jan I)



10. The standard electrode potential E^{O} and its temperature coefficient $\frac{dE^{O}}{dT}$ for a cell are 2V and 5 10 ⁴ VK ¹ at 300 K respectively. The cell reaction is Zn(s) Cu² (aq) Zn² (aq) Cu(s) The standard reaction enthalpy ($_{r}H^{O}$) at 300 K in kJ mol ¹ is, [Use, R 8 JK ¹ mol ¹ and F 96,000 C mol ¹] (2019 Main, 12 Jan I)

	(,,,,,,,
(a) 412.8	(b) 384.0
(c) 206.4	(d) 192.0

- **11.** The reaction, MgO(s) C(s) Mg(s) CO(g), for which $_{r}H^{\circ}$ 491.1 kJ mol⁻¹ and $_{r}S^{\circ}$ 198.0 JK ⁻¹mol⁻¹, is not feasible at 298 K. Temperature above which reaction will be feasible is (a) 2040.5 K (b) 1890.0 K (c) 2380.5 K (d) 2480.3 K
- **12.** The standard reaction Gibbs energy for a chemical reaction at an absolute temperature *T* is given by, ${}_{r}G^{\circ} A BT$ Where *A* and *B* are non-zero constants.

Which of the following is true about this reaction? (2019 Main, 11 Jan II)

- (a) Endothermic if, A = 0 and B = 0
- (b) Exothermic if, B = 0
- (c) Exothermic if, A = 0 and B = 0
- (d) Endothermic if, A = 0
- **13.** For the chemical reaction, $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as

$$_{\rm r}G$$
 (in kJ mol⁻¹) = 120 $\frac{3}{8}$

The major component of the reaction mixture at T is

	•	vomponen			
				(2019 Main, 11	Jan I)
(a)	Y if T	280 K	(b) X if T	350 K	
(c)	X if T	315 K	(d) Y if T	300 K	

14. Two blocks of the same metal having same mass and at temperature T_1 and T_2 respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, S, for this process is (2019 Main, 11 Jan I)

(a)
$${}^{2}C_{p} \ln \frac{(T_{1} - T_{2})^{1/2}}{T_{1}T_{2}}$$
 (b) ${}^{2}C_{p} \ln \frac{T_{1} - T_{2}}{4T_{1}T_{2}}$
(c) $C_{p} \ln \frac{(T_{1} - T_{2})^{2}}{4T_{1}T_{2}}$ (d) ${}^{2}C_{p} \ln \frac{T_{1} - T_{2}}{2T_{1}T_{2}}$

15. The process with negative entropy change is

(2019 Main, 10 Jan II)

- (a) synthesis of ammonia from N_2 and H_2
- (b) dissociation of $CaSO_4(s)$ to CaO(s) and $SO_3(g)$
- (c) dissolution of iodine in water
- (d) sublimation of dry ice
- **16.** An ideal gas undergoes isothermal compression from 5 m³ to 1 m³ against a constant external pressure of 4 Nm². Heat released in this process is used to increase the temperature of 1 mole of Al. If molar heat capacity of Al is 24 J mol⁻¹K⁻¹, the temperature of Al increases by (2019 Main, 10 Jan II) (a) $\frac{3}{2}$ K (b) 1K (c) 2 K (d) $\frac{2}{2}$ K

(a)
$$\frac{3}{2}$$
K (b) 1K (c) 2K (d) $\frac{2}{3}$

17 A process has H 200 J mol⁻¹ and S 40 JK⁻¹ mol⁻¹. Out of the values given below, choose the minimum temperature above which the process will be spontaneous (2019 Main, 10 Jan I)
(a) 20 K
(b) 4 K
(c) 5 K
(d) 12 K

18 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is

(Specific heat of water liquid and water vapour are 4.2 kJ K 1 kg 1 and 2.0 kJK 1 kg 1 ; heat of liquid fusion and vapourisation of water are 334 kJ kg 1 and 2491 kJkg 1 respectively). (log 273 2436, log 373 2.572, log 383 2.583) (2019 Main, 9 Jan II) (a) 9.26 kJ kg 1 K 1 (b) 8.49 kJ kg 1 K 1 (c) 7.90 kJ kg 1 K 1 (d) 2.64 kJ kg 1 K 1

19 Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 $(T_1 \ T_2)$. The correct graphical depiction of the dependence of work done (*W*) on the final volume (*V*) is

(2019 Main, 9 Jan I)



- **20.** The combustion of benzene (l) gives $CO_2(g)$ and $H_2O(l)$. Given that heat of combustion of benzene at constant volume is 3263.9 kJ mol⁻¹ at 25° C; heat of combustion (in kJ mol⁻¹) of benzene at constant pressure will be $(R \ 8.314 \text{ JK}^{-1} \text{ mol}^{-1})$ (2018 Main) (a) 4152.6 (b) 452.46 (c) 3260 (d) 3267.6
- **21.** U is equal to
(a) isochoric work
(c) adiabatic work(2017 Main)(b) isobaric work
(c) adiabatic work(b) isobaric work
(d) isothermal work
- **22.** The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are

 $_{f}G$ [C(graphite)] 0 kJ mol⁻¹

 $_f G$ [C(diamond)] 2.9 kJ mol⁻¹

The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2 10^{6} m³ mol⁻¹. If C(graphite) is converted to C(diamond) isothermally at *T* 298K, the pressure at which C(graphite) is in equilibrium with C(diamond), is (2017 Adv.)

[Useful information : 1 J	$1 \text{ kg m}^2 \text{s}^2$,
1 Pa 1 kg m 1 s 2 ; 1 bar	10 ⁵ Pa]
(a) 58001 bar	(b) 1450 bar
(c) 14501 bar	(d) 29001 bar

23. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm.

In this process, the change in entropy of surroundings (S_{surr}) in JK⁻¹ is (1 L atm 101.3 J) (2016 Adv.) (a) 5.763 (b) 1.013 (c) 1.013 5.763 (d)

24. The following reaction is performed at 298K

 $2NO(g) \quad O_2(g) \Longrightarrow 2NO_2(g)$ The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of NO₂(g) at 298 K? (K_n 1.6 10¹²) (2015 Main)

(a) $R(298) \ln (1.6 \ 10^{12}) - 86600$

(b) 86600
$$R(298) \ln (1.6 \ 10^{12})$$

(c) 86600 $-\frac{\ln (1.6 \ 10^{12})}{R(298)}$

- (d) $0.5[2 86600 R(298) \ln (1.6 10^{12})]$
- **25.** For the process, $H_2O(l)$ $H_{2}O(g)$
 - at T = 100 C and 1 atmosphere pressure, the correct choice is
 - (a) S_{system} 0 and $S_{\text{surrounding}}$ (2014 Adv.) 0

(b) S_{system} 0 and $S_{surrounding}$ 0

(c) S_{system} 0 and $S_{\text{surrounding}}$ 0

(d) S_{system} $0 \text{ and } S_{\text{surrounding}}$ 0

27.

26. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of *q* and *W* for the process will be (0010 14 -)

$(K = \delta)$	314 J / mol K,	ln /.5 2.0	1)		(201)	3 Main)			
(a) q	208 J, W	208 J							
(b) q	208 J, W	208 J							
(c) q	208 J, W	208 J							
(d) q	208 J, W	208 J							
For the	For the process $H_2O(l)$ (1 bar, 373 K) $H_2O(g)$								
(1 bar, 373 K), the correct set of thermodynamic									
parame	ters is				(200	7, 3M)			
(a) <i>G</i>	0, <i>S</i> v	e (b)	G	0, <i>S</i>	ve				
(c) G	ve, S	0 (d)	G	ve,	S ve	5			

28. The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given : $_{r}H_{298K}$ 54.07 kJ mol⁻¹,

 $_{r}S_{298 \text{ K}} = 10 \text{ JK}^{-1} \text{ mol}^{-1} \text{ and } R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1};$ 2.303 8.314 298 5705) (2007, 3M) (b) 10 (c) 95 (d) 100 (a) 5

29. The direct conversion of *A* to *B* is difficult, hence it is carried out by the following shown path

Given that
$$S_{(A \ C)}$$
 50 eu
 $S_{(C \ D)}$ 30 eu
 $S_{(D \ B)}$ -20 euwhere, eu is entropy unit
Then, $S_{(A \ B)}$ is (2006, 3M)
(a) + 100 eu (b) +60 eu
(c) -100 eu (d) -60 eu

30. A monoatomic ideal gas undergoes a process in which the ratio of p to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas? (2006, 3M)

(a)
$$\frac{4R}{2}$$
 (b) $\frac{3R}{2}$ (c) $\frac{5R}{2}$ (d) 0

31. One mole of monoatomic ideal gas expands adiabatically at initial temperature T against a constant external pressure of 1 atm from 1 L to 2 L. Find out the final temperature $(R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1})$ (2005, 1M) (b) $\frac{T}{(2)^{5/3}}$

(c)
$$T = \frac{2}{3 \quad 0.082}$$
 (d) $T = \frac{2}{3 \quad 0.082}$

32. 2 moles of an ideal gas expanded isothermally and reversibly from 1 L to 10 L at 300 K. What is the enthalpy change? (2004, 1M) (a) 4.98 kJ (b) 11.47 kJ (c) -11.47 kJ (d) 0 kJ

33. Spontaneous adsorption of a gas on solid surface is an exothermic process because (2004, 1M)

- (a) H increases for system (b) S increases for gas
- (c) *S* decreases for gas (d) G increases for gas
- 34. One mole of a non-ideal gas undergoes a change of state (2.0 atm, 3.0 L, 95 K) (4.0 atm, 5.0 L, 245 K) with a change in internal energy, E 30.0L-atm. The change in enthalpy (H) of the process in L-atm is (2002. 3M) (a) 40.0 (b) 42.0 (c) 44.0
 - (d) not defined, because pressure is not constant
- **35.** Which of the following statements is false? (2001.1M) (a) Work is a state function
 - (b) Temperature is a state function
 - (c) Change in the state is completely defined when the initial and final states are specified
 - (d) Work appears at the boundary of the system
- **36.** In thermodynamics, a process is called reversible when (2001, 1M)
 - (a) surroundings and system change into each other
 - (b) there is no boundary between system and surroundings
 - (c) the surroundings are always in equilibrium with the system
 - (d) the system changes into the surroundings spontaneously
- **37.** For an endothermic reaction, where *H* represents the enthalpy of the reaction in kJ/mol, the minimum value for the energy of activation will be (1992, 1M)

(a) less than H(b) zero (c) more than H(d) equal to H

38. The difference between heats of reaction at constant pressure and constant volume for the reaction

2	$2C_6H_6(l) + 15O_2$	$12CO_2(g) + 6H_2O(l)$	
at 25	5 C in kJ is		(1991, 1M)
(a)	7.43	(b) + 3.72	
(c)	3.72	(d) + 7.43	

Objective Questions II

(One or more than one correct option)

39. A reversible cyclic process for an ideal gas is shown below. Here, *p*, *V* and *T* are pressure, volume and temperature, respectively. The thermodynamic parameters *q*, *w*, *H* and *U* are heat, work, enthalpy and internal energy, respectively. (2018 Adv.)



The correct options is (are)

- (a) q_{AC} U_{BC} and w_{AB} $p_2(V_2 V_1)$ (b) w_{BC} $p_2(V_2 V_1)$ and q_{BC} H_{AC} (c) H_{CA} U_{CA} and q_{AC} U_{BC} (d) q_{BC} H_{AC} and H_{CA} U_{CA}
- **40.** An ideal gas is expanded form (p_1, V_1, T_1) to (p_2, V_2, T_2) under different conditions. The correct statement(s) among the following is (are) (2017 Adv.)
 - (a) The work done by the gas is less when it is expanded reversibly from V_1 to V_2 under adiabatic conditions as compared to that when expanded reversibly form V_1 to V_2 under isothermal conditions.
 - (b) The change in internal energy of the gas is (i) zero, if it is expanded reversibly with $T_1 = T_2$, and (ii) positive, if it is expanded reversibly under adiabatic conditions with $T_1 = T_2$
 - (c) If the expansion is carried out freely, it is simultaneously both isothermal as well as adiabatic
 - (d) The work done on the gas is maximum when it is compressed irrversibly from (p₂, V₂) to (p₁, V₁) against constant pressure p₁
- **41.** For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by

(2017 Adv.)

- (a) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases
- (b) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surrounding decreases

- (c) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative
- (d) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive
- **42.** An ideal gas in thermally insulated vessel at internal pressure p_1 , volume V_1 and absolute temperature T_1 expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are p_2, V_2 and T_2 , respectively. For this expansion



- **43.** Benzene and naphthalene form an ideal solution at room temperature. For this process, the true statement(s) is (are) (2013 Adv.)
 - (a) G is positive (b) S_{system} is positive (c) $S_{\text{surroundings}} 0$ (d) H 0
- **44.** The reversible expansion ob an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is (are) correct? (2012)



45. For an ideal gas, consider only *P*-*V* work in going from initial state *X* to the final state *Z*. The final state *Z* can be reached by either of the two paths shown in the figure.



[Take S as change in entropy and W as work done]. Which of the following choice(s) is (are) correct? (2012)

(a)
$$S_X \ Z \ S_X \ Y \ S_Y \ Z$$

(b) $W_X \ Z \ W_X \ Y \ W_Y \ Z$
(c) $W_X \ Y \ Z \ W_X \ Y \ Z$
(d) $S_X \ Y \ Z \ S_X \ Y$

- 46. Among the following, extensive property is (properties are) (2010)
 (a) molar conductivity (b) electromotive force (c) resistance (d) heat capacity
- 47. Among the following, the state function(s) is(are)(a) internal energy (2009)
 - (b) irreversible expansion work
 - (c) reversible expansion work
 - (d) molar enthalpy
- **48.** Identify the intensive quantities from the following. (1993, 1M)

(a) enthalpy	(b) temperature
(c) volume	(d) refractive index

Assertion and Reason

Read the following questions and answer as per the direction given below :

- (a) Statement I is true; Statement II is true; Statement II is the correct explanation of Statement I
- (b) Statement I is true; Statement II is true; Statement II is not the correct explanation of Statement I
- (c) Statement I is true; Statement II is false
- (d) Statement I is false; Statement II is true
- **49.** Statement I There is a natural asymmetry between converting work to heat and converting heat to work.

Statement II No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008, 3M)

50. Statement I For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement II At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. (2008, 3M)

51. Statement I The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.Statement II The volume occupied by the

molecules of an ideal gas is zero. (2000, S, 1M)

Passage Based Questions





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- **52.** The pair of isochoric processes among the transformation of states is
 - (a) K to L and L to M
 - (b) L to M and N to K
 - (c) L to M and M to N
 - (d) M to N and N to K
- **53.** The succeeding operations that enable this transformation of states are
 - (a) heating, cooling, heating, cooling
 - (b) cooling, heating, cooling, heating
 - (c) heating, cooling, cooling, heating
 - (d) cooling, heating, heating, cooling

Match the Columns

54. Match the thermodynamic processes given under Column I with the expressions given under Column II.

	Column I		Column II
А.	Freezing of water at 273 K and 1 atm	p.	q = 0
B.	Expansion of 1 mole of an ideal gas into a vacuum under isolated conditions	q.	W 0
C.	Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	r.	$S_{ m sys} = 0$
).	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	S.	<i>U</i> 0
		t.	G = 0

 Match the transformations in Column I with appropriate options in Column II. (2011)

	Column I			Column II
A. $CO_2(s)$	$CO_2(g)$		p.	Phase transition
B. $CaCO_3(s)$	CaO(s)	$CO_2(g)$	q.	Allotropic change
C. 2H	$H_2(g)$		r.	<i>H</i> is positive
D. P _{(white, solid}	P _(red, solid)		s.	S is positive
			t.	S is negative

Fill in the Blanks

- **56.** Enthalpy is an property. (1997, 1M)

58. The heat content of the products is more than that of the reactants in an reaction. (1993, 1M)

59. A system is said to be if it can neither exchange matter nor energy with the surroundings. (1993, 1M)

- **60.** C_p C_V for an ideal gas is
- **61.** The total energy of one mole of an ideal monatomic gas at 27 C iscal. (1984, 1M)

(1984, 1M)

True/False

- **62.** First law of thermodynamics is not adequate in predicting the direction of a process. (1982, 1M)
- 63. Heat capacity of a diatomic gas is higher than that of a monoatomic gas. (1985, 1/2 M)

Integer Answer Type Questions

64. One mole of an ideal gas is taken from *a* to *b* along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is W_s and that along the dotted line path is W_d , then the integer closest to the ratio W_d / W_s is (2010)



Subjective Questions

- **65.** For the reaction, 2CO O_2 2CO_2 ; *H* 560 kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of CO_2 , the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of *U* at 500 K. (1 L-atm = 0.1 kJ) (2006, 3M)
- **66.** 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the H and U. (2004, 2M)
- **67.** C_V value of He is always $\frac{3R}{2}$ but C_V value of H₂ is $\frac{3R}{2}$ at low

temperature and $\frac{5R}{2}$ at moderate temperature and more than

 $\frac{5R}{2}$ at higher temperature. Explain in two or three lines. (2003, 2M)

- **68.** Two moles of a perfect gas undergo the following processes :
 - (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L)

- (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L)
- (c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L)
- (i) Sketch with labels each of the processes on the same p-V diagram.
- (ii) Calculate the total work (W) and the total heat change(Q) involved in the above processes.
- (iii) What will be the values of U, H and S for the overall process? (2002, 5M)
- 69. When 1-pentyne (A) is treated with 4 N alcoholic KOH at 175 C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne (B) and 3.5% of 1, 2-pentadiene (C). The equilibrium was maintained at 175 C. Calculate G for the following equilibria.

$$B \iff A, \qquad G_1 = ?$$

$$B \iff C, \qquad G_2 = ?$$

From the calculated value of G_1 and G_2 indicate the order of stability of (*A*), (*B*) and (*C*). Write a reasonable reaction mechanism showing all intermediates leading to (*A*), (*B*) and (*C*). (2001, 10M)

70. Show that the reaction,
$$CO(g) + \frac{1}{2}O_2(g)$$
 $CO_2(g)$ at

300 K, is spontaneous and exothermic, when the standard entropy change is $0.094 \text{ kJ} \text{ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs' free energies of formation for CO₂ and CO are $-394.4 \text{ and} -137.2 \text{ kJ} \text{ mol}^{-1}$, respectively. (2000, 3M)

- **71.** A sample of argon gas at 1 atm pressure and 27 C expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process C_{V_m} for argon is 12.49 JK ¹ mol ¹. (2000, 4M)
- **72.** A gas mixture of 3.67 L of ethylene and methane on complete combustion at 25 C produces 6.11 L of CO_2 . Find out the amount of heat evolved on burning 1 L of the gas mixture. The heat of combustion of ethylene and methane are 1423 and 891 kJ mol⁻¹ at 25 C. (1991, 5M)
- **73.** An athlete is given 100 g of glucose $(C_6H_{12}O_6)$ of energy equivalent to 1560 kJ. He utilizes 50 per cent of this gained energy in the event. In order to avoid storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ/mol. (1989, 2M)
- **74.** Following statement is true only under some specific conditions. Write the conditions for that in not more than two sentences

"The heat energy q, absorbed by a gas is H." (1984, 1M)

Topic 2 Thermochemistry

Objective Questions I (Only one correct option)

- Enthalpy of sublimation of iodine is 24 cal g⁻¹ at 200°C. If specific heat of I₂(s) and I₂(vap.) are 0.055 and 0.031 cal g⁻¹ K⁻¹ respectively, then enthalpy of sublimation of iodine at 250°C in cal g⁻¹ is (2019 Main, 12 April I)
 - (a) 2.85 (b) 5.7 (c) 22.8 (d) 11.4
- **2.** Given :
 - (i) C(graphite) $O_2(g)$ $CO_2(g)$; $_rH^{\odot}$ x kJ mol⁻¹
 - (ii) C(graphite) $\frac{1}{2}O_2(g)$ $CO_2(g);$ ${}_{r}H^{\circ} \quad y \text{ kJ mol}^{-1}$
 - (iii) $\operatorname{CO}(g) = \frac{1}{2}\operatorname{O}_2(g)$ $\operatorname{CO}_2(g); {}_{\mathrm{r}}H^{\circ} = z \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct? (2019 Main, 12 Jan II)

(a)	у	2z	X	(b) <i>x</i>	У	Z
(c)	Ζ	x	У	(d) <i>x</i>	у	Ζ

3. Given, $C_{(graphite)} = O_2(g)$, $CO_2(g)$;

393.5 kJ mol 1

$$\begin{array}{rl} H_{2}(g) & \frac{1}{2}O_{2}(g) & H_{2}O(l); \\ & & _{r}H & 285.8 \, \text{kJ mol}^{-1} \\ \text{CO}_{2}(g) & 2 \, \text{H}_{2}O(l) & \text{CH}_{4}(g) + 2O_{2}(g); \\ & & _{r}H & 890.3 \, \text{kJ mol}^{-1} \end{array}$$

 $_{r}H$

Based on the above thermochemical equations, the value of $_{r}H$ at 298 K for the reaction, (2017 Main)

(C(graphite)	$2 H_2(g)$	CH	$I_4(g)$ will be		
(a)	78.8 kJ r	nol ¹	(b)	144.0 kJ mol	1	

- (c) 74.8 kJ mol^{-1} (d) $144.0 \text{ kJ mol}^{-1}$
- 4. The heats of combustion of carbon and carbon monoxide are 393.5 and 283.5 kJ mol⁻¹, respectively. The heat of formation (in kJ) of carbon monoxide per mole is (2016 Main)

(a) 676.5	(b) 676.5
(c) 110.5	(d) 110.5

5. For the complete combustion of ethanol, $C_2H_5OH(l) + 3O_2(g)$ $2CO_2(g) + 3H_2O(l)$, the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol⁻¹ at 25°C. Assuming ideality the enthalpy of combustion, _CH, for the reaction will be (R = 8.314 J K⁻¹mol⁻¹) (2014 Main) (a) 1366.95 kJ mol⁻¹ (b) 1361.95 kJ mol⁻¹ (c) 1460.50 kJ mol⁻¹ (d) 1350.50 kJ mol⁻¹

- 6. The standard enthalpies of formation of CO₂(g), H₂O(l) and glucose(s) at 25°C are 400 kJ/mol, 300 kJ/mol and 1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25°C is (2013 Adv.)
 (a) 2900 kJ
 (b) 2900 kJ
 (c) 16.11 kJ
 (d) 16.11 kJ
- 7. Using the data provided, calculate the multiple bond energy $(kJ mol^{-1})$ of a C C bond C₂H₂. That energy is (take the H bond as 350 kJ mol^{-1}) bond energy of a C (2012) $2C(s) H_2(g)$ $C_{2}H_{2}(g);$ $H = 225 \text{ kJ mol}^{-1}$ $H = 1410 \text{ kJ mol}^{-1}$ 2C(s)2C(g); $H = 330 \text{ kJ mol}^{-1}$ $H_2(g)$ 2H(g);(a) 1165 (b) 837 (c) 865 (d) 815
- 8. The species which by definition has zero standard molar enthalpy of formation at 298 K is (2010)
 (a) Br₂(g)
 (b) Cl₂(g)
 (c) H₂O(g)
 (d) CH₄(g)
- 9. The bond energy (in kcal mol⁻¹) of C—C single bond is approximately (2010)
 (a) 1
 (b) 10
 (c) 100
 (d) 1000
- **10.** H_{vap} 30 kJ/mol and S_{vap} 75 Jmol⁻¹K⁻¹. Find the temperature of vapour, at one atmosphere (2004, 1M) (a) 400 K (b) 350 K (c) 298 K (d) 250 K
- **11.** Which of the following reactions defines H_f ?

(a) $C_{(diamond)} + O_2(g)$	$\operatorname{CO}_2(g)$	(2003, 1M)
(b) $\frac{1}{2}$ H ₂ (g) + $\frac{1}{2}$ F ₂ (g)	$\operatorname{HF}(g)$	
(c) $N_2(g) + 3H_2(g)$	$2\mathrm{NH}_3(g)$	
(d) CO $(g) + \frac{1}{2} O_2 (g)$	$CO_2(g)$	

12. The H_f for CO₂(g),CO(g) and H₂O(g) are

393.5, 110.5 and 241.8 kJ mol 1 respectively. Thestandard enthalpy change (in kJ mol 1) for the reaction $CO_2(g) + H_2(g)$ $CO(g) + H_2O(g)$ is(a) 524.1(b) + 41.2(c) 262.5(d) 41.2

Objective Question II

(One or more than one correct option)

- **13.** The following is/are endothermic reaction(s) (1999, 3M)
 - (a) Combustion of methane
 - (b) Decomposition of water
 - (c) Dehydrogenation of ethane to ethylene
 - (d) Conversion of graphite to diamond

14. The thermal dissociation of equilibrium of $CaCO_3(s)$ is studied under different conditions. (2013 Adv.) $CaCO_3(s) \rightleftharpoons CaO(s) \quad CO_2(g)$

For this equilibrium, the correct statement(s) is/are

- (b) K is independent of the initial amount of $CaCO_3$
- (c) K is dependent on the pressure of CO_2 at a given T
- (d) H is independent of the catalyst, if any

Subjective Questions

- **15.** In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increases from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol⁻¹ is (2009)
- **16.** Diborane is a potential rocket fuel which undergoes combustion according to the reaction

 $B_2H_6(g) + 3O_2(g)$ $B_2O_3(s) + 3H_2O(g)$

From the following data, calculate the enthalpy change for the combustion of diborane. (2000, 2M)

$$2B(s) + \frac{3}{2}O_{2}(g) \qquad B_{2}O_{3}(s); \qquad H = 1273 \text{ kJ mol}^{-1}$$
$$H_{2}(g) + \frac{1}{2}O_{2}(g) \qquad H_{2}O(l); \qquad H = 286 \text{ kJ mol}^{-1}$$
$$H_{2}O(l) \qquad H_{2}O(g); \qquad H = 44 \text{ kJ mol}^{-1}$$
$$2B(s) + 3H_{2}(g) \qquad B_{2}H_{6}(g); \qquad H = 36 \text{ kJ mol}^{-1}$$

- **17.** Estimate the average S–F bond energy in SF₆. The values of standard enthalpy of formation of SF₆(g), S(g) and F(g) are : -1100, 275 and 80 kJ mol⁻¹ respectively. (1999, 3M)
- 18. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 K. The enthalpy of formation of CO₂ (g), H₂O (l) and propane (g) are -393.5, 285.8 and 20.42 kJ mol⁻¹ respectively. The enthalpy of isomerisation of cyclopropane to propene is 33.0 kJ mol⁻¹. (1998. 5M)

19. Compute the heat of formation of liquid methyl alcohol in kJ mol⁻¹, using the following data. Heat of vaporisation of liquid methyl alcohol 38 kJ/mol. Heat of formation of gaseous atoms from the elements in their standard states : H 218 kJ/mol, C 715 kJ/mol, O 249 kJ/mol. Average bond energies: (1997, 5M) C—H 415 kJ/mol, C—O 356 kJ/mol, O—H 463 kJ/mol

20. The standard molar enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25 C are 156 and + 49 kJ mol⁻¹ respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25 C is 119 kJ mol⁻¹.

Use these data to estimate the magnitude of the resonance energy of benzene. (1996, 2M)

21. The polymerisation of ethylene to linear polyethylene is represented by the reaction,

$$n [CH_2 CH_2] [CH_2 - CH_2]_{n}$$

where, *n* has large integral value. Given that the average enthalpies of bond dissociation for C C and C C at 298 K are +590 and +311 kJ/mol respectively, calculate the enthalpy of polymerization per mole of ethylene at 298 K. (1994, 2M)

22. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with *x* litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10} .

In order to get the same calorific output, what should be the rate of supply of butane and oxygen? Assume that losses due to incomplete combustion etc., are the same for both fuels and that the gases behave ideally. Heats of combustions:

$CH_4 = 809 \text{ kJ/mol}, C_4H_{10} = 2878 \text{ kJ/mol}$ (1993, 3M)

23. Determine the enthalpy of the reaction,

24. Using the data (all values are in kilocalories per mol at 25 C) given below, calculate the bond energy of C C and C H bonds.

$$\begin{array}{ccc} C(s) & C(g); & H = 1/2 \\ H_2(g) & 2H(g); & H = 104 \\ H_2(g) + \frac{1}{2}O_2(g) & H_2O(l); & H & 68.0 \end{array}$$

$$C(s) + O_2(g)$$
 $CO_2(g);$ H 94.0Heat of combustion of C_2H_6 372.0Heat of combustion of C_3H_8 530.0(1990, 5M)

- **25.** The standard enthalpy of combustion at 25 C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are 241, 3800 and 3920kJ/mol respectively. Calculate the heat of hydrogenation of cyclohexene. (1989, 2M)
- **26.** An intimate mixture of ferric oxide, Fe_2O_3 , and aluminium, Al, is used in solid fuel rockets. Calculate the fuel value per gram and fuel value per cc of the mixture. Heats of formation and densities are as follows:
 - $\begin{array}{ll} H_f(\mathrm{Al}_2\mathrm{O}_3) & 399 \ \mathrm{kcal/mol} \\ H_f(\mathrm{Fe}_2\mathrm{O}_3) & 199 \ \mathrm{kcal/mol} \\ \mathrm{Density} \ \mathrm{of} \ \mathrm{Fe}_2\mathrm{O}_3 & 5.2 \ \mathrm{g/cc}, \ \mathrm{Density} \ \mathrm{of} \ \mathrm{Al} & 2.7 \ \mathrm{g/cc} \end{array}$

(1989, 2M)

⁽a) H is dependent on T

- 27. The standard molar heat of formation of ethane, carbon dioxide and liquid water are 21.1, 94.1 and 68.3 kcal respectively. Calculate the standard molar heat of combustion of ethane. (1986, 2M)
- **28.** The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal/mol respectively. Calculate the enthalpy of formation of HCl gas. (1985, 2M)
- 29. Given the following standard heats of reactions

 (i) heat of formation of water
 (ii) heat of combustion of acetylene
 (iii) heat of combustion of ethylene
 337.2 kcal

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume (25 C). (1984, 4M)

- **30.** The molar heats of combustion of $C_2H_2(g)$, C (graphite) and $H_2(g)$ are 310.62 kcal, 94.05 kcal and 68.32 kcal respectively. Calculate the standard heat of formation of $C_2H_2(g)$. (1983, 2M)
- 31. The standard heats of formation of CCl₄(g), H₂O(g), CO₂(g) and HCl(g) at 298 K are 25.5, 57.8, 94.1 and 22.1 kcal/mol respectively. Calculate H (298 K) for the reaction
 - $CCl_4(g) = 2H_2O(g)$ $CO_2(g) = 4HCl(g)$ (1982, 2M)
- **32.** The enthalpy for the following reactions (H) at 25°C are given below

Thermodynamics and Thermochemistry **111**

(i) $\frac{1}{2}$ H ₂ (g)	$\frac{1}{2}O_2(g)$	OH(g)	Н 10.06	5 kcal
(ii) $H_2(g)$	2H(g)	H	104.18 kcal	
(iii) $O_2(g)$	2O(g)	Н	118.32 kcal	

Calculate the O— H bond energy in the hydroxyl radical. (1981, 2M)

Passage Based Questions

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralisation of a strong acid with a strong base is a constant (57.0 kJ mol⁻¹), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \quad 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

- **33.** Enthalpy of dissociation (in kJ mol⁻¹) of acetic acid obtained from the Expt. 2 is
 (a) 1.0 (b) 10.0 (c) 24.5 (d) 51.4
- **34.** The pH of the solution after Expt. 2 is (a) 2.8 (b) 4.7 (c) 5.0 (d) 7.0

Topic 1 Thermodynamics

1. (c)	2. (a)	3. (b)	4. (a)
5. (d)	6. (c)	7. (b)	8. (a)
9. (a)	10. (a)	11. (d)	12. (d)
13. (c)	14. (c)	15. (a)	16. (d)
17. (c)	18. (a)	19. (c)	20. (d)
21. (c)	22. (c)	23. (c)	24. (d)
25. (b)	26. (a)	27. (a)	28. (b)
29. (b)	30. (a)	31. (c)	32. (d)
33. (c)	34. (c)	35. (a)	36. (c)
37. (c)	38. (a)	39. (b,c)	40. (a, c, d)
41. (a, b)	42. (a,b,c)	43. (b,c,d)	44. (a,c,d)
45. (a,c)	46. (c,d)	47. (a,c,d)	48. (b, d)
49. (b)	50. (d)	51. (b)	52. (b)
53. (c)	54. A r, t; B	p, q, s; C	p, q, s; D p,q, s, t
55. A	p, r, s; B r, s; C	t; D p, q, t	

Answers

56. extensive 57. zero		58. exothermic reaction		
59. isolated	60. <i>R</i>	61. 900	62. T	
63. T	64. (2)	65. (563 kJ)	69. (12.3 kJ)	
70. (285.4 kJ) 71. (116.4 J)	72. (49.82 kJ)	73. (318.96 g)	

Topic 2 Thermochemistry

1. (c)	2. (d)	3. (c)	4. (c)
5. (a)	6. (c)	7. (d)	8. (b)
9. (c)	10. (a)	11. (b)	12. (b)
13. (b,c,d)	14. (a, b, c, d)	15. (9 kJ)	16. (2035 kJ)
17. (309.16	5 kJ)	18. (2091.32	kJ) 19. (116.4 kJ)
20. (152 k	xJ/mol)	21. (32 kJ/mo	ol)
22. (5.46 x)	L/h)	23. (55 kJ)	
25. (121 k	J/mol)	27. (372 kcal	/mol)
28. (22 kc	cal/mol)	29. (41.7 kca	al)
30. (54.2 k	cal)	31. (41.4 kca	1)
32. (121.31	kcal)	33. (1 kJ/mol)	34. (4.7)

Hints & Solutions

Topic 1 Thermodynamics

1. Key Idea Work done during isothermal expansion of an ideal gas is given by the equation. W $p_{\text{ext}} (V_2 \quad V_1)$

According to the given conditions, the expansion is against constant external pressure. So, the work done is given by following formula;

$$W = p_{ext}(V_2 = V_1)$$

1 bar (10L 1L) 9 L bar (:: 1 L bar 100 J)
9 100 J = 0.9 kJ

2. Key Idea The relation between H and U is Η U $n_g RT$ where, n_p n_R n_g number of moles of gaseous products number of moles of gaseous reactants.

The general combustion reaction of a hydrocarbon is as follows :

$$C_x H_y = x - \frac{y}{4} O_2 = x CO_2 - \frac{y}{2} H_2 O_2$$

For heptane, x = 7, y = 16

 $C_7H_{16}(l) + 11O_2(g)$

 $7\mathrm{CO}_2(g)+8\mathrm{H}_2\mathrm{O}(l)$ *n*_o 7 11 4

Now, from the principle of thermochemistry,

$$\begin{array}{ccc} H & U & n_g RT \\ H & U & n_g RT & 4RT \end{array}$$

3. A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. G = 0.

Spontaneity of a process is decided by the value of G, which can be predicted from the Gibb's equation, G = H = T S for positive/negative signs of H and S at any/higher/lower temperature as:

Η	S	Comment on temperature (T)	G	Comment on the process
0	0	at any temp.	0	spontaneous
0	0	at any temp.	0	non-spontaneous
0	0	at lower temp.	0	spontaneous
0	0	at higher temp.	0	spontaneous

4. In the given system, during the compression of a spring the workdone is 10 kJ and 2 kJ of heat is escaped to the surroundings. So, q 2 kJ and W 10 kJ

According to the first law of thermodynamics,

The change in internal energy, U(in kJ) is 8 kJ.

5. q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. q W and option (d), i.e. H-TS are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

6. Given.

 $n = 5 \text{ mol}, T_2 = 200 \text{ K}, T_1 = 100 \text{ K}$ $C_V = 28 \, \mathrm{JK}^{-1} \mathrm{mol}^{-1}$ $U nC_V T$ $nC_V (T_2 \quad T_1)$ 5 mol 28 JK ¹mol ¹ (200 100) K 14,000 J 14 kJ pVnR T $nR(T_2 \quad T_1)$ 5 mol 8JK ¹mol ¹ (200 100)K

7. From the 1st law of thermodynamics,

U q W

- where, U change in internal energy
 - q heat
 - Wwork done

The above equation can be represented for the given processes involving ideal gas as follows:

W

(a) **Cyclic process** For cyclic process, U = 0

q

Thus, option (a) is correct.

(b) Adiabatic process For adiabatic process,

$$\begin{array}{cc} q & 0 \\ U & W \end{array}$$

Thus, option (b) is incorrect.

(c) **Isochoric process** For isochoric process, V = 0. Thus. W 0 (:: Wp V). Vq

Thus, option (c) is correct.

(d) Isothermal process For isothermal process, U = 0Wq

Thus, option (d) is correct.

8. According to Kirchoff's relation,

$$H = n C_p dT \qquad \dots (i)$$

where, H Change in enthalpy.

 C_p Heat capacity at constant pressure.

Given, n = 3 moles, $T_1 = 300$ K, $T_2 = 1000$ K, $C_p = 23 = 0.01$ T On substituting the given values in Eq. (i), we get 1000 = 1000

$$H = 3 (23 \ 0.01 \ T) dT = 3 \ 23 dT = 0.01 \ T \ dT = 300 \ 300 \ 300 \ 3 \ 23 \ T = \frac{0.01 \ T^2}{2} \frac{1000}{300} \ 3 \ 23 \ (1000 \ 300) = \frac{0.01}{2} \ (1000^2 \ 300^2) \ 3 \ [16100 \ 4550] = 61950 \ J = 62 \ kJ$$

9. For diatomic ideal gases,

$$C_V \quad \frac{f}{2}R \text{ and } C_p \quad \frac{f}{2} \quad 1 R$$

where, f degree of freedom

f translational degree of freedom rotational degree of freedom

3 2 5 [at normal temperature]

The explanation of various plots are as follows.

- (a) We know that, C_p is heat capacity at constant pressure. Thus, it does not vary with the variation in pressure. Hence, plot given in option (a) is incorrect.
- (b) In this plot, C_V first increases slightly with increase in temperature and then increases sharply with temperature. The sharp increase is due to increase in degree of freedom. Thus, plot given in option (b) is correct.
- (c) For ideal gases,

Internal energy (U) T

Thus, as temperature increases internal energy also increases. As temperature increases further degree of freedom also increases thus, there is slight variation in the graph. First translational degree of freedom is present followed by rotational and vibrational degree of freedom. Hence, plot given in option (c) is also correct.

- (d) C_V is heat capacity at constant volume. Thus, it does not vary with variation in volume. Hence, plot given in option (d) is correct.
- 10. Given,

$$E \qquad 2V, \quad \frac{dE}{dT} \qquad 5 \quad 10^{-4} V K^{-1}$$

According to Gibbs-Helmholtz equation,

$$\begin{array}{cccc} G & H & T & S & \dots(i) \\ G & nFE & & & \dots(ii) \\ \end{array}$$

Also, $G nFE_{cell}$ On substituting the given values in equation (ii), we get

$$G = 2.96000 \text{ C mol}^{-1} 2 \text{ V}$$

[:: n = 2 for the given reaction] 4 96000J mol⁻¹

Now, $S \quad nF \quad \frac{dE}{dT}$

or
$$S = 2$$
 96000C mol⁻¹ (5 10 ⁴VK⁻¹)

96 JK 1 mol 1

Thus, on substituting the values of G and S in Eq. (i), we get 384000 J mol⁻¹

$$H = 300 \text{ K} (96 \text{ JK} \text{ }^{1}\text{mol} \text{ }^{1})$$

$$H = 384000 \text{ } 28800 \text{ Jmol} \text{ }^{1}$$

$$412800 \text{ Jmol} \text{ }^{1}$$

$$412.800 \text{ kJ mol} \text{ }^{1}$$

11. According to Gibbs-Helmholtz equation,

$${}_{r}G {}_{r}H {}_{T}{}_{r}S$$
For a reaction to be feasible (spontaneous)

$${}_{r}G {}_{0} {}_{r}H {}_{T}{}_{r}S < 0$$
Given, ${}_{r}H {}_{0}A {}_{1}S < 0$
Given, ${}_{r}H {}_{0}A {}_{1}B {}_$

Above 2480.3 K reaction will become spontaneous.

12. According to Gibb's Helmholtz equation,

$$_{r}G$$
 $_{r}H$ T $_{r}S$
 $_{r}G$ A BT

On comparing above two equations, we get,

$$A$$
 H and S B

We know that, if H is negative, reaction is exothermic and when it is positive, reaction is endothermic.

If A = 0, i.e. positive, reaction is endothermic.

13. For a given value of T,

Given.

- (i) If $_{r}G$ becomes < 0, the forward direction will be spontaneous and then the major and minor components will be *Y* and *X* respectively.
- (ii) If ${}_{r}G$ becomes > 0, the forward direction will be non-spontaneous and then the major and minor components will be X and Y respectively.

(a)
$$_{r}G$$
 120 $\frac{3}{8}$ 280 15

i.e. $_{r}G = O 0$, major component X;

(b)
$$_{r}G$$
 120 $\frac{5}{8}$ 350 11.25

i.e.
$$_{r}G$$
 0, major component Y

c)
$$_{r}G$$
 120 $\frac{3}{8}$ 315 1.875

i.e. $_{r}G$ 0, major component X

(d)
$$_{r}G$$
 120 $\frac{5}{8}$ 300 7.5

i.e. $_{r}G$ 0, major component X

final temperature
$$T_f = \frac{T_1 - T_2}{2}$$

for the 1st block,
$$S_{I} = C_{p} \ln \frac{T_{f}}{T_{1}}$$

for the 2nd block, $S_{II} = C_{p} \ln \frac{T_{f}}{T_{2}}$
When brought in contact with each other,
 $S = S_{I} = S_{II} = C_{p} \ln \frac{T_{f}}{T_{1}} = C_{p} \ln \frac{T_{f}}{T_{2}}$
 $C_{p} \ln \frac{T_{f}}{T_{1}} = \frac{T_{f}}{T_{2}} = C_{p} \ln \frac{T_{f}^{2}}{T_{1}T_{2}}$
 $C_{p} \ln \frac{\frac{T_{I}}{T_{1}} - \frac{T_{2}}{T_{2}}}{T_{1}T_{2}} = C_{p} \ln \frac{(T_{1} - T_{2})^{2}}{4T_{1}T_{2}}$

15. The explanation of all the options are as follows : (a) $N_2(g) = 3H_2(g) = 2NH_3(g)$,

$$n_g 2 (1 3) 2$$

So, *S* is also negative (entropy decreases)

(b)
$$CaSO_4(s)$$
 CaO(s) SO₃(g),
 n_g (1 0) 0 1
So, S ve

- (c) In dissolution, S ve because molecules/ions of the
- solid solute (here, iodine) become free to move in solvated/dissolved state of the solution,

$$I_2(s) \xrightarrow{Water} I_2(aq)$$

(d) In sublimation process, molecules of solid becomes quite free when they become gas,

$$CO_2(s)$$
 $CO_2(g)$
Dry ice

- So, S will be positive.
- **16.** It is an irreversible isothermal compression of an ideal gas.

(i) $dE \quad dq \quad p(V_f \quad V_i)$

- where, dE Internal energy change
 - dq amount of heat released 0 da p(V = V)

$$\begin{array}{l} 0 \quad aq \quad p(v_f \quad v_i) \\ [\because dE \quad 0 \text{ for an isothermal process}] \end{array}$$

$$dq \quad n \quad C \qquad T \text{ (for Al)}$$

16 J 1 mol 24 J mol
1
 K 1 T

$$T = \frac{16}{24} \text{ K} = \frac{2}{3} \text{ K}$$

17. G H T S

(ii)

The process will be spontaneous, when G ve, i.e. |T S| | H|

Given :
$$H = 200 \text{ Jmol}^{-1}$$
 and $S = 40 \text{ JK}^{-1} \text{mol}^{-1}$

$$T = \frac{|H|}{|S|} = \frac{200}{40} = 5 \text{ K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

18. The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:

9.26 kJ kg
1
K 1

19. For isothermal reversible expansion,

$$|W| = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{V}{V_i}$$

where, V final volume, V_i initial final.

or
$$|W| = nRT \ln V = nRT \ln V_i$$

On comparing with equation of straight line, y mx c, we get slope m nRT

intercept
$$nRT \ln V_i$$

Thus, plot of |W| with $\ln V$ will give straight line in which slope of $2(T_2)$ is greater than slope of $1(T_1)$ which is given in all options.

Now, if V_i 1 then y intercept $(nRT V_i)$ becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y-intercept goes above and other y-intercept goes below. Thus, option (b) and (d) are incorrect.

If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y-intercept. But they cannot give same y-intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then *y*-intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

20. Key idea Calculate the heat of combustion with the help of following formula

 $H_p \quad U \quad n_g RT$

where, H_p Heat of combustion at constant pressure

- U Heat at constant volume (It is also called E)
- n_g Change in number of moles (In gaseous state).
- R Gas constant; T Temperature.

From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g)$$
 $6CO_2(g) + 3H_2O(l)$

Change in the number of gaseous moles i.e.

$$n_g = 6 = \frac{15}{2} = \frac{3}{2} \text{ or } 1.5$$

Now we have n_g and other values given in the question are U = 3263.9 kJ/mol

- Т 25 С 273 25 298 К
- $R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$
- So, H_p (3263.9) (1.5) 8.314 10⁻³ 298 3267.6 kJ mol⁻¹
 - 5207.0 KJ 11101
- 21. According to first law of thermodynamics, U q W q p V In isochoric process (V 0), U q In isobaric process (p 0), U q In adiabatic process (q 0), U W In isothermal process (T 0) and U 0 U is equal to adiabatic work.

$$dG \quad dU \quad pdV \quad Vdp \quad TdS \quad SdT \quad Vdp \quad SdT$$

$$[:: dU \quad pdV \quad dq \quad TdS]$$

$$dG \quad Vdp \text{ if isothermal process } (dT \quad 0)$$

$$G \quad V \quad p$$

Now taking initial state as standard state

Now (ii)-(i) gives,

$$(V_d \quad V_{gr}) \quad p \quad G_d \quad G_{gr} \quad (G_{gr} \quad G_d)$$

At equilibrium, $G_d = G_{gr}$

$$(V_{gr} \quad V_d) \quad p \quad G_d \quad G_{gr} \quad 2.9 \quad 10^3 \text{ J}$$

$$p = \frac{2.9 \times 10^3}{2 \times 10^6} Pa = \frac{29}{2} = 10^8 Pa = \frac{29000}{2} bar$$
$$p = p_0 = \frac{29000}{2} = 1 = \frac{29000}{2} = 14501 bar$$

23. By first law, $E \ Q \ W$ For isothermal expansion, $E \ 0$ $Q \ W$ Also, $S_{surr} \frac{Q_{irrev}}{T} \frac{(3 \ 101.3) \text{ J}}{300 \text{ K}} \frac{303.9}{300} 1.013 \text{ JK}^{-1}$

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24. For the given reaction,
$$2NO(\alpha) \rightarrow O(\alpha) \rightarrow 2NO(\alpha)$$

Given,
$$G_f(\text{NO}_2) \leftarrow 2\text{NO}_2(g)$$

 $G_f(\text{NO}_2) \approx G_f(\text{NO}_2)$
 $K_p = 1.6 \quad 10^{12}$
Now, we have,

25. PLAN This problem is based on assumption that total entropy change of universe is zero.

At 100°C and 1 atmosphere pressure,

For equilibrium,

 $H_2O(l) \xrightarrow{} H_2O(g) \text{ is at equilibrium.}$

and $S_{\text{system}} = S_{\text{surrounding}} = 0$ As we know during conversion of liquid to gas entropy of

system increases, in a similar manner entropy of surrounding decreases.

$$S_{\text{system}}$$
 0 and $S_{\text{surrounding}}$ 0

26. The process is isothermal expansion, hence

$$\begin{array}{rcrcr} q & W \\ E & 0 \\ W & -2.303 \; nRT \; \log \frac{V_2}{V_1} \\ & 2.303 \; 0.04 \; 8.314 \; 310 \; \log \frac{335}{50} \\ & 208 \; J \\ q \; & 208 \; J \\ W \; & 208 \; J \; (expansion \; work) \end{array}$$

27. At transition point (373 K, 1.0 bar), liquid remains in equilibrium with vapour phase, therefore G 0. As vaporisation occur, degree of randomness increases, hence S 0.

28. G H T S =
$$-54.07 10^3 ext{ J} - 298 \times 10 ext{ J}$$

 $-57.05 \times 10^3 ext{ J}$
Also, G 2.303 RT log K
 $\log K \frac{G}{2.303 ext{ RT}}$
 $\frac{57.05 10^3}{5705} 10$

29. Entropy is a state function hence,

$$S_{A \ B} = S_{A \ C} = S_{C \ D} = S_{D \ B}$$

50 eu + 30 eu + (- 20 eu)
60 eu

30. Given,
$$\frac{p}{V} = 1$$
 $p = V$...(i)

Also from first law : $dq = C_V dT$ pdV For one mole of an ideal gas : pVRT pdVVdp

From (i)

Substituting in Eq. (ii) gives

$$2pdV \quad RdT \qquad pdV \quad \frac{R}{2}dT$$

$$dq \quad C_V dT \quad \frac{R}{2}dT$$

$$\frac{dq}{dT} \quad C_V \quad \frac{R}{2} \quad \frac{3}{2}R \quad \frac{R}{2} \quad 2R$$

pdV

31. For an irreversible, adiabatic process;

$$0 \quad C_V (T_2 \quad T_1) \quad p_e (V_2 \quad V_1)$$

Substituting the values

$$C_V(T \quad T_2) \quad 1(2 \quad 1) \text{ atm L}$$

 $T \quad T_2 \quad \frac{1}{C_V} \quad \frac{2}{3R} \quad T_2 \quad T \quad \frac{2}{3 \quad 0.082}$

RdT

Vdp

32. In case of reversible thermodynamic process,

$$H nC_p T$$

- Process is isothermal, T 0 Η 0
- **33.** For a spontaneous process G
 - Also; G H T S

For adsorption of gas on solid surface, S 0. Therefore, in order to be G = 0, H must be negative.

34. Η U(pV) 30 2(5 3) 5(4 - 2) = 44 L atm.

- **35.** Work is not a state-function, it depends on path followed.
- **36.** In a reversible thermodynamic process, system always remains in equilibrium with surroundings.

37.



Minimum value of activation energy must be greater than H.

38. H E
$$n_g RT$$
 H E $n_g RT$ 3RT
3 8.314 298 7433 J = -7.43 kJ

39. In the given curve AC represents isochoric process as volume at both the points is same i.e., V_1

Similarly, AB represents isothermal process (as both the points are at T_1 temperature) and BC represents isobaric process as both the points are at p_2 pressure.

Now (i) for option (a)

$$q_{AC} = U_{BC} = nC_V(T_2 - T_1)$$

where, *n* number of moles

 C_{ν} specific heat capacity at constant volume

However,
$$W_{AB} = p_2(V_2 = V_1)$$
 instead
 $W_{AB} = nRT_1 \ln \frac{V_1}{V_2}$

So, this option is incorrect.

(ii) For option (b)

 q_{BC} H_{AC} $nC_p(T_2 T_1)$

where, C_p specific heat capacity at constant pressure Likewise,

 T_1)

$$W_{BC} \qquad p_2 (V_1 \quad V_2)$$

Hence, this option is correct. (iii) For option (c)

as
$$nC_p(T_2 \ T_1) \ nC_V(T_2$$

so $H_{CA} \ U_{CA}$

and
$$q_{AC}$$
 U_{BC}
Hence, this option is also correct.

(iv) For option (d)

Although
$$q_{BC}$$
 H_{AC}
but H_{CA} U_{CA}
Hence, this option is incorrect

40.

...(ii)



Irreversible compression Reversible compression

Maximum work is done on the system when compression occur irreversibly and minimum work is done is reversible compression.



(b)



AB is isothermal and AC is adiabatic path. Work done is area under the curve. Hence, less work is obtained in adiabatic process than in isothermal

(c) It is incorrect. In adiabatic expansion cooling is observed, hence $U nC_v T = 0$.

(d)
$$q = 0$$
 (adiabatic), $W = 0$ (Free expansion)
Hence, $U = 0$, $T = 0$ (Isothermal)

41.
$$S_{surr} = \frac{H}{T_{surr}}$$

For endothermic reaction, if T_{surr} increases, S_{surr} will increase. For exothermic reaction, if T_{surr} increases, S_{surr} will decrease.

42. PLAN This problem includes concept of isothermal adiabatic irreversible expansion.

Process is adiabatic because of the use of thermal insolution therefore, q = 0

 $\therefore p_{\text{ext}} = 0$

 $w p_{\text{ext}} V 0 V 0$ Internal energy can be written as

$$U \quad q \quad W \quad 0$$

The change in internal energy of an ideal gas depends only on temperature and change in internal energy (U) 0 therefore, T 0 hence, process is isothermal and

 $\begin{array}{ccc} T_2 & T_1 \\ \text{and} & p_2 V_2 & p_1 V_1 \\ \end{array}$

(d) $p_2V_2 = p_1V_1$ is incorrect, it is valid for adiabatic reversible process.

Hence, only (a), (b) and (c) are correct choices.

43. PLAN When an ideal solution is formed process is spontaneous thus According to Raoult's law, for an ideal solution

 $\begin{array}{cccc} H & 0, \ V_{\min} & 0 \\ \\ From the relation \\ G & H & T & S \\ \\ Since, & H & 0 \\ G & ve \\ i.e. \ less \ than \ zero. \ and \ S_{surroundings} & 0 \end{array}$

Therefore, S_{sys} ve i.e. more than zero.

- **44.** (a) Since, change of state (p_1, V_1, T_1) to (p_2, V_2, T_2) is isothermal therefore, $T_1 = T_2$.
 - (b) Since, change of state (p₁, V₁, T₁) to (p₃, V₃, T₃) is an adiabatic expansion it brings about cooling of gas, therefore, T₃ T₁.
 - (c) Work done is the area under the curve of *p-V* diagram. As obvious from the given diagram, magnitude of area under the isothermal curve is greater than the same under adiabatic curve, hence *W*_{isothermal} *W*_{adiabatic}

(d) $U nC_v T$

In isothermal process, U = 0 as T = 0In adiabatic process, $U = nC_v(T_3 = T_1) = 0$ as T_3

 $U_{\rm isothermal} \qquad U_{\rm adiabatic}$ NOTE Here only magnitudes of work is being considered otherwise both works have negative sign.

45. (a) Entropy is a state function, change in entropy in a cyclic process is zero.

Therefore,
$$S_X \ _Y \ S_Y \ _Z \ S_Z \ _X \ 0$$

 $S_Z \ _X \ S_X \ _Y \ S_Y \ _Z \ S_Y \ _Z$

Analysis of options (b) and (c)

Work is a non-stable function, it does depends on the path followed. $W_Y = 0$ as V = 0.

Therefore, $W_X = _Y = _Z = W_X = _Y$. Also, work is the area under the curve on *p*-*V* diagram.



As shown above $W_X = W_Y = W_X = W_X = W_X = W_X = W_X$ but not equal to $W_X = Z$.

- **46.** Resistance and heat capacity are mass dependent properties, hence they are extensive.
- **47.** Internal energy, molar enthalpy are state function. Also, reversible expansion work is a state function because between given initial and final states, there can be only one reversible path.
- **48.** Intensive properties are those property which do not depends on amount of sample. Both temperature and refractive index are intensive properties while enthalpy and volumes are extensive properties as they depends on amount of sample.
- **49.** Statement I is true, it is statement of first law of thermodynamics.

Statement II is true, it is statement of second law of thermodynamics. However, Statement II is not the correct explanation of statement I.

50. Statement I is false. At equilibrium

$$G \quad 0, G \quad 0.$$

Statement II is true, spontaneous direction of reaction is towards lower Gibbs free energy.

51. Statement I is true.

$$\begin{array}{cccc} dq & dE & p_{\text{ext}} dV & 0 \\ T & 0 & \\ dE & 0 \ ; & p_{\text{ext}} & 0 \\ p_{\text{ext}} dV & 0 \end{array}$$

Statement II is true. According to kinetic theory of gases, volume occupied by molecules of ideal gas is zero.

However, Statement II is not the correct explanation of Statement I.

52. L M At constant V — isochoric,

$$N = K$$

 T_1 .

53. PLAN By Boyle's law at constant temperature, $p = \frac{1}{W}$

By Charles' law at constant pressure, V = TProcess taking place at Constant temperature — isothermal Constant pressure — isobaric Constant volume — isochoric Constant heat — adiabatic

Κ	L	At constant <i>p</i> , volume increases	thus, heating
L	М	At constant <i>V</i> , pressure decreases	thus, cooling
М	Ν	At constant <i>p</i> , volume decreases	thus, cooling
Ν	Κ	At constant <i>V</i> , pressure increases	thus, heating

54. (A) r, t; (B) p, q, s; (C) p, q, s; (D) q, s, t

(A) $H_2O(l) \xrightarrow{0 C_x} H_2O(s)$

- q 0, W 0 (expansion) S_{svs} 0 (solid state is more ordered than liquid state)
 - U < 0; G = 0 (At equilibrium)
- (B) q = 0 (isolated), W = 0 ($p_{ext} = 0$)

$$\begin{array}{cccc} \mathbf{S}_{\mathrm{sys}} & \mathbf{0} & \because V_2 & V_1 \\ U & \mathbf{0} & \because q & W & \mathbf{0} \end{array}$$

$$G \quad 0 :: p_2 \quad p_1$$

(C) q = 0 (isothermal mixing of ideal gases at constant p) $W \quad 0:: \quad U \quad 0; q \quad 0, \quad S_{svs} \quad 0$

$$\therefore V_2 V_1, U 0$$

 $\therefore T = 0$

 $G \quad 0$:: mixing is spontaneous.

(D) q = 0 (returning to same state and by same path)

W = 00 (same initial and final states) $S_{\rm sys}$

0 U

$$T_i$$
, T_f , G 0

55. (A) $CO_2(s)$ $CO_2(g)$

> It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence *S* is positive.

(B)
$$CaCO_3(s)$$
 $CaO(s) + CO_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, S > 0.

- (C) 2H $H_2(g)$ A new H—H covalent bond is being formed, hence, H = 0. Also, product is less disordered than reactant, S < 0.
- (D) Allotropes are considered as different phase, hence P_(red, solid) is a phase transition as well as P_(white, solid) allotropic change.

Also, red phosphorus is more ordered than white phosphorus, S 0.

- 56. Extensive : Enthalpy is an extensive property while molar enthalpy is an intensive property.
- **57.** Zero: $W \ p \ V \ 0 \because V \ 0$
- **58.** Exothermic reaction.
- 59. Isolated This system neither exchange matter nor energy with surroundings.

- **60.** R: For an ideal gas, C_p C_V R
- **61.** 900 cal : $E = \frac{3}{2}RT = \frac{3}{2}$ 2 300 cal
- 62. True First law deals with conservation of energy while second law deals with direction of spontaneous change.
- 63. True Diatomic gases have more degree of freedom than a monatomic gas.
- **64.** Work done along dashed path |W| = pV

4 1.5 1 1
$$\frac{2}{3}$$
 2.5 8.65 L atm

Work done along solid path $W = nRT \ln \frac{V_2}{V_1} = p_1 V_1 \ln \frac{V_2}{V_1}$

2 2.3
$$\log \frac{5.5}{0.5}$$
 2 2.3 $\log 11$ 4.79
 $\frac{W_d}{W} = \frac{8.65}{4.79} = 1.80$ 2

65. (pV)Н U U

$$-560 - 1$$
 30 $0.1 = -563$ kJ

66. Uq = W

For adiabatic process, q = 0, hence U = W

$$W p(V) p(V_2 V_1) U 100 (99 100) 100 bar mI H U (pV)$$

where, $pV \quad p_2V_2 \quad p_1V_1$

67. He is monatomic, so it has only three degree of freedom (translational only) at all temperature hence, C_V value is always $\frac{3}{2}$ R.

Hydrogen molecule is diatomic, has three translational, two rotational and one vibrational degree of freedom. The energy spacing between adjacent levels are in the order of :

translational < rotational < vibrational

At lower temperature only translational degree of freedom contribute to heat capacity while at higher temperature rotational and vibrational degree of freedom starts contributing to heat capacity.



Total work done $W_1 \quad W_2 \quad W_3$ $20 \text{ L atm} \quad 0 \quad 20 \ln 2$ -6.14 atmFrom first law : $q \quad E \quad (W) \quad W$ $(\because E \quad 0 \text{ for cyclic process})$ $q \quad 6.14 \text{ L atm} = 622.53 \text{ J}$

(iii) All the states function, U, H and S are zero for cyclic process.

69. At equilibrium : $B \rightleftharpoons A$ 95.2% 1.3%

$$K_1 \quad \frac{13}{952}$$
$$B \stackrel{\longrightarrow}{\longleftrightarrow} C$$
$$95.2\% \quad 3.5\%$$
$$K_2 \quad \frac{35}{952}$$

$$G_1 \qquad RT \ln K_1$$

$$-8.314$$
 448 2.303 log $\frac{13}{952} = 16$ kJ

$$G_2 \qquad RT \ln K_2 \\ -8.314 \quad 448 \quad 2.303 \log \frac{35}{952} \\ 12.3 \text{ kJ}$$

70.
$$_{r}G$$
 $_{f}G$ (products) – $_{f}G$ (reactants)

$$-394.4 - (-137.2) = -257.2 \text{ kJ} < 0$$

The above negative value of G indicates that the process is spontaneous.

Also,
$$G$$
 H T S
 H G T S
 $-257.2 + 300 (-0.094)$
 -285.4 kJ < 0

71. Given : C_V 12.49 C_p 20.8

$$\frac{C_p}{C_V}$$
 1.66

In case of reversible adiabatic expansion :

$$TV^{-1} \text{ constant}$$

$$\frac{T_2}{T_1} = \frac{V_1}{V_2}^{-1} = \frac{V_1}{V_2}^{-0.66}$$

$$T_2 = T_1 = \frac{V_1}{V_2}^{-0.66}$$

$$300 = \frac{1}{2}^{-0.66} = 189.86 \text{ K}$$

$$H = nC_p = T$$

$$= \frac{1}{0.082} = 300 = 20.8 \quad (189.86 = 300) \text{ J}$$

$$= -116.4 \text{ J}$$

72. Let the mixture contain x litre of CH_4 and 3.67 x litre of ethylene.

$$CH_4 + O_2 \qquad CO_2$$

$$C_2H_4 + O_2 \qquad 2CO_2$$

$$3.67 \quad x \qquad 2 (3.67 \quad x)$$
Given : $x = 2 (3.67 \quad x) \quad 6.11 \text{ L}$

$$x = 1.23 \text{ L}$$
Volume of ethylene = 2.44 L
Total moles of gases in 1 litre $\frac{pV}{RT} = \frac{1}{0.082} \frac{1}{298} = 0.04$
Also, CH₄ and ethylene are in 1 : 2 volume (or mole) ratio, moles
of CH₄ = $\frac{0.04}{3}$ and moles of ethylene $= \frac{2}{3} = \frac{0.04}{3}$
Heat evolved due to methane $= \frac{0.04}{3} = 891 = 11.88 \text{ kJ}$
Heat evolved due to ethylene $= \frac{2}{3} = 11.88 \text{ kJ}$
Total heat evolved on combustion of 1.0L gaseous mixture at 25°C is $11.88 + 37.94 = 49.82 \text{ kJ}$

73. Moles of H₂O needs to perspire $\frac{1560}{2 \ 44}$ 17.72

Weight of water needs to perspire 17.72 18 318.96 g

74. At constant pressure, q = H.

Topic 2 Thermochemistry

1. Key Idea When q is the amount of heat involved
in a system then at constant pressure
$$q \quad q_p$$
 and $C_p \quad T \quad H$

Given reaction :

 $I_2(s)$ $I_2(g)$

Specific heat of $I_2(s) = 0.055$ cal g⁻¹ K⁻¹.

 $\label{eq:specific heat of I_2(vap) 0.031 cal g^{-1}K^{-1}.$

Enthalpy (H_1) of sublimation of iodine 24 cal g⁻¹

If q is the amount of heat involved in a system then at constant pressure $q = q_p$ and

$$H \quad C_p \quad T$$

$$H_2 \quad H_1 \quad C_p(T_2 \quad T_1)$$

$$H_2 \quad H_1 \quad C_p(T_2 \quad T_1)$$

$$H_2 \quad 24 \quad (0.031 \quad 0.055) (250 \quad 200)$$

 H_2 24 (0.024) (50) 24 1.2 22.8 cal/g

Thus, the enthalpy of sublimation of iodine at 250 $^{\circ}\mathrm{C}$ is 22.8 cal/g.

2. Second equation given in this question is wrong. Hence, No answer in correct.

If corrected second equation is given,

i.e.
$$C(graphite) = \frac{1}{2}O_2(g) = CO(g)$$

and if we take the above reaction in consideration then x y z will be the answer as:

(ii) C(graphite) $\frac{1}{2}O_2(g)$ CO(g), _rH ykJ/mol

(iii) CO(g) $\frac{1}{2}$ O₂(g) CO₂(g), _rH zkJ/mol

Summing up both the equation you will get equation (i): C(graphite) $O_2(g)$ $CO_2(g)$, $_rH$ x kJ/mol Hence, x, y and z are related as:

x y z

3. Based on given $_{r}H$

$$_{f}H = H_{\rm CO_2}$$
 393.5 kJ mol⁻¹ ...(i)

$$_{f}H = H_{\rm H_{20}} = 285.8 \,\rm kJ \, mol^{-1} \qquad ...(ii)$$

$$_{f}H = H_{02} = 0.00$$
 (elements) ...(iii)

Required thermal reaction is for $_{f}H$ of CH₄

Thus, from III

890.3 [
$$_{f}H$$
 (CH₄) + 2 $_{f}H$ (O₂)]
[$_{f}H$ (CO₂) 2 $_{f}H$ (H₂O)]
 $_{f}H$ (CH₄) + 0] [393.5 2 285.5]
 $_{f}H$ (CH₄) = 74.8 kJ / mol

4.
$$C(s) + O_2(g)$$
 $CO_2(g)$; *H* 393.5 kJ mol⁻¹ ...(i)
 $CO + \frac{1}{2}O_2$ $CO_2(g)$; *H* 283.5 kJ mol⁻¹ ...(ii)

On subtracting Eq. (ii) from Eq. (i), we get

C (s) +
$$\frac{1}{2}O_2(g)$$
 CO(g);
H (393.5 283.5)kJ mol⁻¹
110 kJ mol⁻¹(approx.)

5.
$$C_2H_5OH(l) + 3O_2(g)$$
 $2CO_2(g) + 3H_2O(l)$
 U 1364.47 kJ/mol
 H U n_gRT
 n_g 1
 $H = 1364.47 + \frac{1 8.314 298}{1000}$

[Here, value of *R* in unit of J must be converted into kJ] 1364.47 2.4776 1366.9476 kJ/mol or 1366.95 kJ/mol

6. PLAN $_{c}H$ (Standard heat of combustion) is the standard enthalpy change when one mole of the substance is completely oxidised. Also standard heat of formation ($_{f}H$) can be taken as the standard of that substance.

$$\begin{array}{cccc} H_{\rm CO_2} & {}_{f}H \ ({\rm CO_2}) & 400 \ {\rm kJ \ mol}^{-1} \\ \\ H_{\rm H_2O} & {}_{f}H \ ({\rm H_2O}) & 300 \ {\rm kJ \ mol}^{-1} \\ \\ H_{\rm glucose} & {}_{f}H \ ({\rm glucose}) & 1300 \ {\rm kJ \ mol}^{-1} \\ \\ H_{\rm O_2} & {}_{f}H \ ({\rm O_2}) & 0.00 \\ \\ {\rm C_6H_{12}O_6(s)} & 6 \ {\rm O_2(g)} & 6 \ {\rm CO_2(g)} & 6 \ {\rm H_2O(l)} \end{array}$$

$$_{c}H$$
 (glucose) 6[$_{f}H$ (CO₂) $_{f}H$ (H₂O)]
[$_{f}H$ (C₆H₁₂O₆) 6 $_{f}H$ (O₂)]
6[400 300] [1300 6 0]
2900 kJ mol⁻¹
Molar mass of C₆H₁₂O₆ 180 g mol⁻¹

Thus, standard heat of combustion of glucose per gram

1

To solve such problem, students are advised to keep much importance in unit conversion. As here, value of R (8.314 J K ¹ mol ¹) in JK ¹ mol ¹ must be converted into kJ by dividing the unit by 1000.

7. For calculation of C C bond energy, we must first calculate dissociation energy of C_2H_2 as $C_2H_2(g) = 2C(g) + 2H(g) = \dots(i)$

Using the given bond energies and enthalpies :

$$C_2H_2(g) = 2C(g) + 2H(g); H = 225 \text{ kJ} \dots(ii)$$

 $2C(s) = 2C(g); H = 1410 \text{ kJ} \dots(iii)$
 $H_2(g) = 2H(g); H = 330 \text{ kJ} \dots(iv)$
Adding Eqs. (ii), (iii) and (iv) gives Eq. (i).
 $C_2H_2(g) = 2C(g) + 2H(g); H = 1515 \text{ kJ}$
 $1515 \text{ kJ} = 2 \text{ (C H) BE} \text{ (C C) BE}$
 $2 = 350 \text{ (C C) BE}$

(C C) BE 1515 700 815 kJ / mol

- 8. Elements in its standard state have zero enthalpy of formation. Cl_2 is gas at room temperature, therefore H_f of $Cl_2(g)$ is zero.
- **9.** C—C bond energy is approximately 100 kcal.

10.
$$T = \frac{H_{\text{vap}}}{S_{\text{vap}}} = \frac{30,000}{75} = 400 \text{ K}$$

11.
$$\frac{1}{2}$$
H₂(g) + $\frac{1}{2}$ F₂(g) HF(g)

Here H Standard molar enthalpy of formation of HF(g).

12. $CO_2(g) + H_2(g)$ $CO(g) + H_2O(g)$

H
$$_{f}H$$
 (products) $_{f}H$ (reactants)
- 110.5 - 241.8 - (- 393.5) = + 41.20 kJ

13.
$$H_2O$$
 $H_2 + \frac{1}{2}O_2$, $H = 0$

It is reverse of combustion of $H_2(g)$, hence endothermic.

$$C_2H_6 \qquad C_2H_4 \quad H_2; \qquad H \quad 0$$

Here, more stable (saturated) hydrocarbon is being transformed to less stable (unsaturated) hydrocarbon, hence endothermic.

$$C_{(gr)}$$
 $C_{(d)}$, H 0

More stable allotrope is being converted to less stable allotrope.

14. PLAN Heat of reaction is dependent on temperature (Kirchhoff's equation) in heterogeneous system, equilibrium constant is independent on the molar concentration of solid species.

Heat of reaction is not affected by catalyst. It lowers activation energy.

$$CaCO_3(s) \rightleftharpoons CaO(s) \quad CO_2(g)$$

By Kirchhoff's equation,

$$H_{2}(\text{at }T_{2}) = H_{1}(\text{at }T_{1}) = C_{p}(T_{2} = T_{1})$$

H varies with temperature. Thus, (a) is correct.

 $K p_{CO_2}$

K is dependent on pressure of CO₂ but independent of molar concentration of CaCO₃. Thus, (b) and (c) are correct. At a given temperature, addition of catalysis lowers activation energy, H remaining constant. Thus, (d) is also correct.



- E_a Activation energy in absence of catalyst
- E_a Activation energy in presence of catalyst

15. Temperature rise
$$T_2$$
 T_1 298.45 - 298 = 0.45 K
q heat capacity $T = 2.5$ 0.45 = 1.125 kJ
Heat produced per mole $\frac{1.125}{3.5}$ 28 9 kJ

16.
$$H_r$$
 H_f (B₂O₃)+3 H_f (H₂O)- H_f (B₂H₆)
 H_f (H₂O)(g) H_f (H₂O)(l) + 44 - 242 kJ
 H_r - 1273 - 3 242 - 36
- 2035 kJ

17. $SF_6(g)$ S(g) + 6F(g)

H
$$H_f$$
 (products) H_f (reactants)
275 + 6 80 + 1100 = 1855 kJ
Average S—F bond energy $\frac{1855}{6} = 309.16$ kJ/mol

18. Given : Cyclopropane Propene (C_3H_6) ; H 33 kJ

Propene (C₃H₆)
$$\frac{9}{2}$$
 O₂ $3CO_2(g) + 3H_2O(l);$
 $H - 3 (393.5 + 285.8) - 20.42 = -2058.32 \text{ kJ}$
Adding :
Cyclopropane $\frac{9}{2}$ O₂ (g) $3CO_2(g) + 3H_2(g);$

$$\begin{array}{cccc} H & H_1 & H_2 \\ & 33 & (\ 2058.32) \text{kJ} \\ H & 2091.32 \text{ kJ} \end{array}$$

19. Given : CH₃OH (g) CH₃OH (l); H 38 kJ
C (g) + 4H (g) + O (g) CH₃OH (g);
H (3 415 356 463)

$$\therefore$$
 H H₁ H₂ 2064 kJ
C(g) C(g); H 715 kJ

Adding : C (gr) + 2H₂ (g) +
$$\frac{1}{2}$$
 O₂ (g) CH₃OH(*l*)
H 266 kJ/mol
 $\frac{1 \ 1.25}{0.082 \ 300}$ 20.8 (189.86 300) J
116.4 J

20.

$$+ H_{2} \longrightarrow ; H = -119$$

$$+ 3H_{2} \longrightarrow ; H = -119 ; H = -119 ; H = -119 ; H = -119 × 3 = -357 \text{ kJ} (Theoretical)$$

$$-357 \text{ kJ} = H_f \text{ (cyclohexane)} \quad H_f \text{ (C}_6 \text{H}_6\text{)}$$

$$H_f (C_6H_6)_{\text{Theoretical}} = -156 + 357 = 201 \text{ kJ}$$

Resonance energy H_f (exp.) H_f (Theoretical)

21. Per mole of ethylene polymerized, one C C bond is broken and two C—C bonds are formed.

22. At same temperature and pressure, equal volumes contain equal moles of gases.

Let 1.0 L of CH_4 contain '*n*' mol x L of CH_4 contain *nx* mol Heat evolved in combustion by x L $CH_4 = 809 nx kJ$

Now, 2878 kJ energy is evolved from 1 mole $\frac{1}{n}$ L C₄H₁₀.

809 *nx* kJ energy will be evolved from $\frac{809 \text{ } nx}{2878 \text{ } n}$ L of C₄H₁₀

0.28
$$x L$$
 of C₄H₁₀

Also, the combustion reaction of butane is

$$C_4 H_{10} + \frac{13}{2} O_2$$
 $4CO_2 + 5H_2O$
Rate of supply of oxygen $\frac{13}{2}$ 0.28 x 3

= 5.46 x L/h

23. First we need to determine heat of combustion of C_3H_8 .

$$3C(gr) + 4H_2(g)$$
 $C_3H_8(g)$ H_f 103 kJ
- 103 kJ = -3 393 - 4 285.80 - H_{comb} (C₃H₈)

 $H_{\text{comb}}(C_3H_8) = -2219.20 \text{ kJ}$ H_{r} $H_{\rm comb}$ (reactants) H_{comb} (products) -2219.20 - 285.80 + 1560 + 890= -55 kJ**24.** Let *x* kcal be the C—C bond energy and *y* kcal be the C—H bond energy per mole. $2C(gr) + 3H_2(g)$ $C_2H_6(g);$ $H = -2 \quad 94 - 3 \quad 68 + 372$ -20 kcal - 20 kcal 2 172 3 104 BE (C₂H₆) BE (C_2H_6) 676 kcal Similarly, $3C(gr) + 4H_2(g)$ $C_{3}H_{8}(g);$ $H = -3 \quad 94 - 4 \quad 68 + 530$ = -24 kcal -24 kcal 3 172 4 104 BE (C₃H₈) $BE(C_3H_8)$ 956 kcal $BE(C_2H_6)$ 676 kcal x 6y Also, ...(i) BE (C₃H₈) 956 kcal 2x = 8y...(ii) Solving Eqs. (i) and (ii) gives *y* 99 kcal (C—H) BE x 82 kcal (C—C) BE + H₂ -25. $H = H_{\text{comb}}$ (reactants) $H_{\rm comb}$ (products) = -3800 - 241 - (-3920)= - 121 kJ/mol **26.** $Fe_2O_3(s) + 2Al(s)$ $Al_2O_3(s) + 2Fe(s)$ H_r H_f (products) H_f (reactants) = -399 - (-199)= -200 kcal Mass of reactants 56 2 16 3 27 2 214 g $\frac{200}{214} \quad 0.93 \text{ kcal/g}$ Fuel value/gram Volume of reactants $\frac{160}{5.2}$ cc + $\frac{54}{2.7}$ cc = 50.77 cc Fuel value/cc $\frac{200}{50.77}$ 3.94 kcal/cc 27. H H_f (products) H_f (reactants) -2 94.1 -3 68.3 -(-21.1)- 372 kcal/mol

28.
$$\frac{1}{2}$$
 H₂(g) + $\frac{1}{2}$ Cl₂(g) HCl(g); H_f
H_f BE (reactants) BE (products)
 $\frac{1}{2}$ (104 58) 103 = - 22 kcal/mol
29. C₂H₂ + H₂ C₂H₄
H H_{comb} (reactants) H_{comb} (products)
- 310.6 - 68.3 - (-337.2)
- 41.7 kcal

30. The standard state formation reaction of $C_2H_2(g)$ is :

$$2C(g) + H_{2}(g) \qquad C_{2}H_{2}(g); \qquad H_{f}$$

$$H_{r} \qquad H_{comb} \text{ (reactants)} \qquad H_{comb} \text{ (products)}$$

$$-2 \quad 94.05 - 68.32 - (-310.62)$$

$$54.2 \text{ kcal} = H_{f} (C_{2}H_{2})$$

31.
$$H_r$$
 ${}_{f}H$ (products) ${}_{f}H$ (reactants)
-94.1 + 4 (-22.1) - (-25.5 - 2 57.8)
= -41.4 kcal

32. *H* BE (reactants) BE (products)

$$10.06 \quad \frac{1}{2} (104.18) \quad \frac{1}{2} (118.32)$$
 BE (O H)
BE (O—H) = 121.31 kcal

33. Let $C JK^{-1}$ be the heat capacity of calorimeter. Mass of solution 200 mL 1 g mL¹ 200 g Heat evolved in Expt.1 57 1000 0.1(mol) 5700 J 5700 J (200 4.2 C) 5.7 1000 200 4.2 C ...(i) Let x kJ/mol is heat evolved in neutralisation of acetic acid. x 1000 0.10 (200 4.2 C) 5.6 x 100 200 4.2 C ...(ii) 5.6 From (i) and (ii) : x = 56 kJ/molEnthalpy of ionisation of acetic acid 56 (57) 1 kJ/mol **34.** $CH_3COOH + NaOH$ CH₃COONa + H₂O 200 mmol 100 mol 0 0 100 mmol 0 100 mmol A buffer is now formed. [H⁺][CH₃COO] [H] K_a [CH₃COOH] [∵[CH₃COOH] [CH₃COO]] pH p K_a log (2 10⁵) 5 log 2 4.7