



CHEMISTRY

BOOKS - NAGEEN CHEMISTRY (ENGLISH)

CHEMICAL THERMODYNAMICS

Example

1. State whether each of the following will increase or decrease the total

energy content of the system.

heat transferred to the surroundings.



2. State whether each of the following will increase or decrease the total

energy content of the system.





3. State whether each of the following will increase or decrease the total

energy content of the system.

Work done on the system.

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4. Heat transferred from surroundings to the system will increase or

decrease the total energy content of the system.



5. A system absorbs 400 J of heat and does work equivalent to 150 J on the surroundings. Calculate the change in the internal energy of the system.

6. A gas expands against a constant pressure of 1 atm from a volume of 5L to 10L. During the process, system absorbs 400 J of heat from the surroundings. Calculate the change in the internal energy of the system.

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7. A 5.0 litres cylinder contained 10 moles of hydrogen gas at 27°C. Due to leakage, entire gas escaped into the atmosphere. The atmospheric pressure is 1.0 atm. Calculate the work done by the gas assuming hydrogen to be an ideal gas.

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8. The enthalpy change (ΔH) for the reaction

 $N_2(g)+3H_2(g)
ightarrow 2NH_3(g)$

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is -92.38 kJ at 298 K. What is \Delta U at 298 K ? \left(R=8.314 j K^{-1} mol^{-1}
ight)
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9. The difference between heats of reaction at constant pressure and constant volume for the reaction.

 $2C_6H_6(l) + 15O_2(g)
ightarrow 12CO_2(g) + 6H_2O(l)$

at $25^{\,\circ}\,C$ in kJ is

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10. The heat of combustion of methane $CH_4(g)$ is measured in a bomb calorimeter at 298.2 K and is found to be $-885.50 k Jmol^{-1}$. Find the value of enthalpy change Δ H.

11. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane (i) at constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter system is $17.7kJK^{-1}(R = 8.314JK^{-1}mol^{-1})$.



12. 10 moles of a gas are heated at constant volume from $20^{\circ}C$ to $30^{\circ}C$. Calculate the change in the internal energy of the gas. The molar heat capacity of the gas at constant pressure, $C_p = 6.82 cal K^{-1} mol^{-1}$ and $R = 1.987 cal K^{-1} mol^{-1}$.

13. A gas expands from $3dm^3$ to $5dm^3$ against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10 moles of water at temperature 290 K. Calculate the final temperature of water. Specific heat of water = $4.184JK^{-1}q^{-1}$.

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14. The enthalpy change for the transition of liquid water to steam $\Delta_{
m vap}H$ is 40.8 kJ mol^{-1} at $100^{\,\circ}C$. Calculate the entropy change $(\Delta_{
m vap}S)$ for the process.

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15. What will be the melting point of KCl if enthalpy change for the reaction is 7.25 J mol^{-1} and entropy change is $0.007 \text{ J K}^{-1} \text{mol}^{-1}$?



16. Calculate the entropy change (ΔS) for the following reaction at $25^{\circ}C$.

$$SO_2(g)+rac{1}{2}O_2(g)
ightarrow SO_3(g)$$

The absolute entropies at $25^{\circ}C$ and 1 atm pressure for $SO_2(g), O_2(g)$ and $SO_3(g)$ are 248.5, 205.0 and 256.2 J K^(-1) mol^(-1)` respectively.



17.1 mole of α -tin at 1 atm and $13^{\circ}C$ changes to 1 mole of β -tin at 1 atm and $13^{\circ}C$. If the enthalpy of transition is $2090Jmol^{-1}$, calculate the entropy of transition.



18. For the reaction, $NH_4Cl(s) o NH_3(g) + HCl(g)$ at $25^\circ C$, enthalpy change $\Delta H = +\,177kJmol^{-1}$ and entropy change

 $\Delta S=+285 Jmol^{-1}K^{-1}.$ Calculate the free energy change $\Delta G~~{
m at}~~25^{\,\circ}C$ and predict whether the reaction is spontaneous or not.

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19. At $0^{\,\circ}\,C$, ice and water are in equilibrium and $\Delta H = 6.0 k J mol^{-1}$ for

the process

 $H_2O(s) \Leftrightarrow H_2O(l)$

What will be ΔS and ΔG for the conversion of ice to liquid water?

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20. The enthalpy change (ΔH) for the reaction

$$Ag_2O(s) \Leftrightarrow 2Ag(s) + rac{1}{2}O_2(g)$$

is $30.54kJmol^{-1}$ and entropy change (ΔS) is $0.06kJK^{-1}mol^{-1}$ at 1 atm. Calculate the temperature at which ΔG is equal to zero. Also predict the direction of reaction at a temperature below the calculated temperature.



21. For a reaction, $K_p = 1.8 imes 10^{-7}$ at 300K. What is the value of ΔG°

at this temeprature ?

$$(R=8.314 J K^{-1} mol^{-1})$$

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22. Calculate the standard free energy change for the following reaction

$$Zn(s)+Cu^{2+}(aq)
ightarrow Zn^{2+}(aq)+Cu(s)$$

Given :
$$\Delta_f G^\circ \left[C u^{2\,+} \left(a q
ight)
ight] = 65.0 k J mol^{-1}$$

$$\Delta_{f}G^{\,\circ}\left[Zn^{2\,+}\left(aq
ight)
ight]=\ -\,147.2kJmol^{\,-\,1}$$

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23. Calculate the equilibrium constant for the following reaction at 298

 $2H_2O(l)
ightarrow 2H_2(g) + O_2(g)$

Given : $\Delta_f G^{\circ}[H_2O(l)] = -273.2kJmol^{-1}R = 8.314Jmol^{-1}K^{-1}$.

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24. Calculate the enthalpy change for the reaction

$$H_2(g)+rac{1}{2}O_2(g)
ightarrow H_2O(g)$$

if the bond energies of H - H, O = O and O - H bonds are 104, 118

and 11 kcal mol^(-1)` respectivley.

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25. Calculate the standard enthalpy change for the reaction

$$CH_4(g)+2O_2(g)
ightarrow CO_2(g)+2H_2O(l),$$

given that the standard heatds of formation of $CH_4(g, CO_2(g) \text{ and } H_2O(l)$ are $-74.91mol^{-1}$, $-394.12kJmol^{-1}$ and $-286.31kJmol^{-1}$

respectivley.



26. Calculate the standard heat of formation of $C_2H_5OH(l)$ from the following data:

(a)
$$C_2 H_5 OH(l) + 2 O_2(g) o 2 C O_2(g) + 3 H_2 O(l)$$
,

 $\Delta H^{\,\circ}~=~-~1366.5 kJ$

(b) $\Delta_{f} H^{\,\circ}[CO_{2}]=\,-\,393.5 k Jmol^{\,-1},$

 $\Delta_{f} H^{\,\circ}[H_{2}O(l)] = \ -\ 285.5 k Jmol^{-1}.$

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27. Calculate the calorific value of methane if it burns according to the

equation

$$CH_4(g) + 2O_2(g)
ightarrow CO_2(g) + 2H_2O(l), \Delta H = -890.0 kJ$$

28. An average person eats carbohydrates equivalent to 0.350 kg of glucose and 0.200 kg of fats every day. The person needs about 10000 kJ per day. If the body consumes carbohydrates preferentially, how much will his weight increase per year assuming that only 50% of the excess fats are excreted. Give that the heat of combustion of glucose is 2900 kJ and combustion of fats produces energy equivalent to $39000kJkg^{-1}$?

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29. Calculate G° for conversion of oxygen to ozone 3/2 O2 \rightleftharpoons O3(g) at 298

Kp, if K for this conversion is 2.47 x 10-29 in standard pressure units.

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30. What would be the heat released when 0.5 mole of HCl in solution is

neutralised by 0.25 mole of KOH?

31. What would be the heat released when 0.6 mole of HNO_3 in solution is mixed with 0.4 mole of NaOH ?



34. Calculate the heat of formation of glucose from the following data,

$$egin{aligned} C(s) &+ O_2(g) o CO_2(g), \Delta H = &- 395.0 kJ \ H_2(g) &+ rac{1}{2} O_2(g) o H_2O(l), \Delta H = &- 269.4 kJ \ C_6 H_{12} O_6(s) &+ 6 O_2(g) o 6 CO_2(g) + 6 H_2O(l), \Delta H = &- 2900 kJ \end{aligned}$$

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35. The molar heats of combustion of $C_2H_2(g)$, C (graphite), and H_2 are

-310.62kcal, -94.05 kcal and -68.32 kcal respectively. Calculate the

standard heat of formation of $C_2H_2(g)$.

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36. Calculate the heat of the following reaction at $25^{\circ}C$.

 $C_2H_4(g)+H_2(g)
ightarrow C_2H_6(g)$

The heats of combustion of ethylene, hydrogen and ethane are-1410 kJ,

-286.2 kJ and -1560.6 kJ respectively at $25^{\circ}C$.



37. Calculate the heat of formation of anhydrous Al_2Cl_6 from the following data:

(i) $2Al+6HCl(aq)
ightarrow Al_2Cl_6(aq)+3H_2(g), \Delta H=-239.76kcal$

(ii) $Al_2Cl_6(s)+aq
ightarrow Al_2Cl_6(aq), \Delta H=-153.69kcal$

(iii) $H_2(g)+Cl_2(g)
ightarrow 2HCl(g), \Delta H=-44kcal$

(iv) $HCl(g) + aq
ightarrow HCl(aq), \Delta H = -17.31 kcal$

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38. Calculate the C—C bond energy from the following data:

 $2C(ext{graphite})+3H_2(g)
ightarrow C_2H_6(g), \Delta H=~-84.67kJ$

 $C(ext{graphite}), \
ightarrow C(g) \Delta H = 716.7 kJ$

 $H_2(9g), \
ightarrow 2H(g)\Delta = 435.9kJ$

Assume 416 as the C - H bond energy.

39. Calculate the enthalpy of the following reaction :

$$CH_2=CH_2(g)+H_2(g)
ightarrow CH_3-CH_3(g)$$

The bond energies of C-H, C-C, C=C and H-H bonds are 414, 347, 615 and 435 kJ mol^{-1} respectively.

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Review Exercises

1. Define thermodynamics. Describe the significance and limitations of thermodynamics.

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2. What do you understand by the terms system and surroundings?

Discuss with examples the various types of systems.





6. Define Extensive properties.

7. What type of systes are the following system?

Hot tea placed in a cup.

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8. What type of systes are the following system?

Hot tea placed in a sealed metallic tea pot.

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9. What type of systes are the following system?

Hot tea placed in a thermos flask.



10. The equilibrium constant at 298 K for the reaction Cu(s) + 2Ag+ (aq)

 \Rightarrow Cu2+ (aq) + 2Ag(s) is 2.0 × 1015 . The concentrations of Cu2+ and Ag+



14. Assign the proper sign to q and w in the following cases :

Surroundings transfer 25kJ of energy to the system.

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15. Assign the proper sign to q and w in the following cases :

15 kJ of energy is transferred to the system by doing work on it.

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16. Assign the proper sign to q and w in the following cases :

30 kJ of energy is lost by the system on account of the work done by the

system on the surroundings.

17. What do you understand by pressure-volume work? Derive an expression for it.

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18. Caclulate DeltaU, internal enegry change of a system, if it absorbs 25

kJ of heat and does 5kJ of work.

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19. A system absorbs 20kJ heat and also does 10kJ of work. The net

internal enegry of the system



20. Predict the mode of energy transference in the following processe.

(i) Cooking of food



23. Classify the following into open, closed and isolated system.

Boiling of milk in a pan.

24. Classify the following into open, closed and isolated system.

Boiling tea kept in a thermos.

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25. Classify the following into open, closed and isolated system.

Hot food kept in a sealed metallic container.



26. Explain first law of thermodynamics. What'is its physical significance ?



27. Define internal energy and enthalpy of a system.

28. Why is the enthalpy considered more useful than internal energy in

chemical reactions ?

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29. Derive the following equation :

 $\Delta H = \Delta U + (\Delta n) RT$

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30. One mole of an ideal gas is expanded from a volume of 3L to 5L

under a constant pressure of 1 atm. Calculate the work done by the gas.

31. During a process, a system absorbs 710 kJ of heat and does 250 J of

work. Calculate the change in the internal energy of the system.

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32. Two moles of an ideal gas at 2 atm and $25^{\circ}C$ are compressed isothermally to one third of its volume by an external pressure of 6 atm. Calculate q, w and ΔU .

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33. A system has internal energy U_1 . If 500 J of heat is supplied to it and at the same time it does 300 J of work. Calculate the internal energy of the system in the new state,

34. Heat of combustion of $CH_4(g)$ at constant volume and at 298 K has been found to be $-885kJmol^{-1}$, calculate the enthalpy of its combustion under constant pressure condition ($R = 8.31JK^{-1}mol^{-1}$).

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35. When 2 g of benzene are burnt in a bomb calorimeter, the heat produced is 83.6 kJ at 298 K. Calculate the enthalpy of combustion of benzene.

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36. The enthalpy change (ΔH) of the reaction at 298 K

 $C_2H_5OH(l)+3O_2(g)
ightarrow 2CO_2(g)+3H_2O(l)$

is found to be -326.7 kcal. Calculate ΔE for the given reaction.

37. $400cm^3$ of a gas are compressed to half of its volume by applying a pressure of 0.5 atm. During the process 6.5 J of heat flows out to the surroundings. Calculate ΔU of the system.

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38. Calculate the work done (w) and internal energy change (ΔU), when one mole of water at $100^{\circ}C$ vaporises against an atmospheric pressure of 1 atm assuming ideal gas behaviour. Heat of vapourisation of water at $100^{\circ}C$ is $1020calmol^{-1}$.

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39. Calculate the work done in calories when 5 moles of an ideal gas are compressed isothermally and reversibly from a pressure of 1.5 atm to 15 atm at $27^{\circ}C$.

40. In a reaction 2.5KJ of heat is released from the system and 5.5 KJ of

work is done on the system.Calculate 'DeltaU'.





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45. Define the term 'entropy'. How does $T\Delta S$ determine the spontaneity

of a process?

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46. What is meant by the term 'free energy'? What was the necessity of

introducing such a function ?

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47. State the second law of thermodynamics. Predict the sign of ΔS in the following change at constant temperature and pressure. Give reason



49. What inferences do you draw on the basis of the values of Gibbs free energy change? How is it related to the enthalpy and entropy changes of a system at constant temperature and pressure?



50. The enthalpy change for the transition of liquid water to steam $\Delta_{
m vap} H$ is 40.8 kJ mol^{-1} at $100^\circ C$. Calculate the entropy change





51. At 373 K, the entropy change for the transition of liquid water to steam (ΔS_{vap}) is $109JK^{-1}mol^{-1}$. Calculate the enthalpy change $(\Delta_{\text{vap}}H)$ for the process.



52. For the chemical equilibrium

 $PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g) \ \ ext{at} \ \ 298K, K_c = 1.8 imes 10^{-7}.$

Calculate $\Delta_r G^{\Theta}$ for the forward reaction $R=8.31 J K^{-1} {
m mol}^{-1}$

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53. For a reaction, $K=1.958 imes 10^{-4}$ at 400 K, what is the value of

$$\Delta G^{\,\circ}$$
 at this temepratuure ? $(R=8.314 J K^{-1} mol^{-1}).$

54. Calculate ΔG° for the reaction $2HCl(g) + F_2(g) \rightarrow 2HF(g) + Cl_2(g)$ at $25^{\circ}C$ at Given : $\Delta_f G^{\circ}[HCl(g)] = -95.30 k J mol^{-1}$. $\Delta_f G^{\circ}[HF(g)] = -273 k J mol^{-1}$. Also calculate the equilibrium constant the reacton at $25^{\circ}C$. Given, gas constant $R = 8.314 J K^{-1} mol^{-1}$.

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55. Calculate the equilibrium constant for the following reaction at 298 K and 1 atm pressure.C(graphite)+H2O(I)=CO(g)+H2(g) Given : 'Delta_f H^@, [H_2O (I)] = -286.0 kJ mol^(-1), Delta_f H^@ [CO (g)] = - 110.5 kJ mol^(-1), DeltaS^@ at298Kf or thereaction = $252.6Jk^{-1}mol^{-1}$. Gas constant $R = 8.31Jk^{-1}mol^{-1}$. 56. Calculate the equilibrium constant for the following reaction at 298 K and 1 atm pressure.C(graphite)+H2O(l)=CO(g)+H2(g) Given : 'Delta_f H^@, [H_2O (l)] = -286.0 kJ mol^(-1), Delta_f H^@ [CO (g)] = - 110.5 kJ mol^(-1), DeltaS^@ at298Kf or thereaction = $252.6Jk^{-1}mol^{-1}$. Gas constant $R = 8.31Jk^{-1}mol^{-1}$.

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57. Calculate the standard free energy change for the reaction

 $4NH_3(g)+5O_2(g)
ightarrow 4NO(g)+6H_2O(l)$

Given that the standard free energy of formation $(\Delta_f G^\circ)$ for $NH_3(g)NO(g)$ and $H_2O(l)$ are -16.8, + 86.7 and $-237.2kJmol^{-1}$ respectively. Predict the feasibility of the above reaction at the standard state.

58. Calculate the standard entropy change for the reaction $X \Leftrightarrow Y$ if the value of $\Delta H^\circ = 28.40 kJ$ and equilibirum constant is 1.8×10^{-7} at 298 K.

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59. Calculate the entropy change when 20.0 g of ice changes to liquid water at 0°C. The heat of fusion is $80.0calg^{-1}$.



60. From the following values of ΔH and ΔS , decide whether or not these reaction are feasible at 298 K.

Reaction A : $\Delta H = -10.5 imes 10^3 Jmol^{-1}, \Delta S = +31 JK^{-1} mol^{-1}$

Reaction B : $\Delta H = -11.7 imes 10^3 Jmol^{-1}, \Delta S = -105 JK^{-1} mol^{-1}$

61. Determine standard free energy ΔG° at $25^\circ C$ for the reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ Given: $\Delta H^\circ = -91.8kJ, \Delta S^\circ = -198JK^{-1}$

62. For a hypothetical reaction nX o mY, the value of $\Delta H = -133 kJ$ and $\Delta S = -145 JK^{-1}$. Calcualte the value of ΔG at 700 K.

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63. For a hypothetical reaction nX o mY, the value of $\Delta H = -133 kJ$ and $\Delta S = -145 JK^{-1}$. Calcualte value of $\Delta S_{
m surr.}$ and $\Delta S_{
m univ}$

64. Compute the standard free energy of the reaction at $27^{\circ}C$ for the

combustion of methane

 $CH_4(g)+2O_2(g)
ightarrow CO_2(g)+2H_2O(l)$

using the following data :

Species	CH4 (g)	O2 (g)	CO ₂ (g)	H ₂ O(/)
$\Delta_{f}H^{\circ}$ (kj mol ⁻¹)	-74.8	-	-393.5	-285.8
5° (J K ⁻¹ mol ⁻¹)	186	205	214	70

Also comment on the feasibility of the reaction.

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65. The reaction

 $CH_3COOH(l) + C_2H_5OH(l) \Leftrightarrow CH_3COOC_2H_5(l) + H_2O(l)$

was carried out at 27°C by taking one mole each of the reactants. The reaction reached equilibrium when 2/3rd of the reactants were consumed. Calculate the free energy change for the reaction.
66. A system loses 120) of heat and does 80 J of work. Calculate the

change in the internal energy of the system.



67. Calculate the enthalpy change for the reaction

 $CH_2=CH_2(g)+H_2(g0
ightarrow CH_3-CH_3(g).$

The bond energies of C-C, C-H, H-H and C = C bonds are 83

kcal, 99 kcal 104 kcal and 145 kcal respectivley.



68. Sort out the exothermic and endothermic reactions among the following:

(i)
$$C(s) + 2H_2(g) o CH_4(g), \Delta H = -17.89cal$$

(ii) $CO(g) + rac{1}{2}O_2(g) o CO_2(g) = +284.5kJ$
(iii) $2HCl(g) o 2H(g) + 2Cl(g), \Delta H = +857kJ$
(iv) $Cl_2(g) + 242kJ o 2Cl(g)$





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70. Calculate the standard heat of formation of propane if its heat of combustion is $-2220.2kjmol^{-1}$. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are -394.12 and $-286.31kJmol^{-1}$ respectively.

71. When 14.9 g of solid KCl is dissolved in large excess of water, the amount of heat liberated is 3.72 kJ. Calculate the heat of solution of KCl.



72. what is entropy change for reaction 2H2(g) + O2(g) ----?2H2O(I). Standard entropies of H2(g), O2(g) and H2O(I) are 126.6, 201.20,68.0 J/k mol respectively

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73. Calculate the amount of heat liberated when $500cm^3$ of $\frac{N}{10}H_2SO_4$

react with $400 cm^3$ of $rac{N}{15}$ NaOH.

74. The standard molar heat of formation of ethane, carbon dioxide and water (liquid) are -21.1, -94.1 and -68.3 kcal respectively. Calculate the standard heat of the following reaction :

 $2C_2H_6(g)+7O_2(g)
ightarrow 4CO_2(g)+6H_2O(l)$

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75. The $\Delta H^{\,\circ}$ for the reaction

 $H_2(g)+I_2(g)
ightarrow 2HI(g)$

is +53.6 kJ. Mention whether the reaction is exothermic or endothermic

and calculate the standard heat of formation of HI.

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76. The heat of combustion of butane is 2658 kl. A cylinder of LPG gas (containing only butane) is assumed to contain 14.2 kg of butane. If a



78. Sucrose undergoes combustion as

 $C_{12}H_{22}O_{11} + 12O_2(g)
ightarrow 12CO_2(g) + 11H_2O(l), \Delta H = -5643kJ$

How much energy will be liberated when 3.42 g of sucrose are burnt ?

79. Calculate the heat of formation of methanol (CH_3OH) from thhe following data:

 $egin{aligned} CH_3OH(l) &+ rac{3}{2}O_2(g) o CO_2(g) + 2H_2O(l), \Delta = &-726kJ \ C(s) + O_2(g) o CO_2(g), \ \Delta H &= &-394kJ \ H_2(g) + rac{1}{2}O_2(g) o H_2O(l), \Delta H &= &-286kJ \end{aligned}$

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80. Calculate the heat of formation of $MgCO_2$ (s) from the following data

$$egin{aligned} C(ext{graphite}) &+ O_2(g) o CO_2(g), \Delta H = -393.5 kJ \ 2Mg(s) &+ O_2(g) o 2MgO(s), \Delta H = -1203.6 kJ \ MgO(s) &+ CO_2(g) o MgCO_3(s), \Delta H = -117.7 kJ \end{aligned}$$

81. Calculate the bond energy of H-Cl bond, given that the bond energies of H–H, Cl—Cl bonds are $433kJmol^{-1}$ and $242kJmol^{-1}$ respectivly. The ΔH_f for HCl is -91 $kJ mol^{-1}$.



82. Calculate the heat of combustion of ethyl alcohol from the following

data :

(i) Heat of formation of ethyl alcohol = -64.1 kcal

(ii) Heat of formation of water = -68.5 kcal

(iii) Heat of formation of CO2 =- 94.3 kcal.

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83. What would be the complications if Hess's law were not true?

84. What is bond enthalpy and how is it calculated?



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$$egin{aligned} \mathbf{2}.\, H_2(g) &+ rac{1}{2}O_2(g) o H_2O(l), \Delta H = \ -\ 286 kJ \ 2H_2(g) &+ O_2(g) o 2H_2O(l), \Delta H = \ldots kJ \end{aligned}$$

$$egin{aligned} \mathbf{3.}\, H_2(g) + I_2(g) &
ightarrow 2HI(g), \Delta H = 52.2kJ \ 2HI(g) &
ightarrow H_2(g) + I_2(g), \Delta H = kJ \end{aligned}$$

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4.
$$CH_4(g) + 2O_2(g) o CO_2(g) + 2H_2O(g), \Delta H = -809kJ$$

The calorific value of 1 kg of $CH_4(g)$ is kJ/kg.

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5.
$$C(s)
ightarrow C(g), \Delta H = 716.7 kJ$$

 ΔH is the heat of of graphite.

6.
$$N_2(g) + 3H_2(g) o 2NH_3(g), \Delta H = -92.3kJ$$

 $2NH_3(g) o N_2(g) + 3H_2(g), \Delta H = \dots kJ$



Very Short Answer Type Questions

1. Define thermodynamics.

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2. What type of systes are the following system?

Hot tea placed in a thermos flask.

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3. Sort out the intensive and extensive properties among the following:

Temperature, mass, specific heat, density, enthalpy, entropy, concentration, free energy.

4. Which of the following are not state functions ?

Temperature, entropy, heat, work, enthalpy, internal energy.

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5. Distinguish between isobaric and isochoric process.
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6. What is the sign convention for heat ?
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7. A system transfers 20 kJ of heat to the surroundings. Write the value

of q for both the system and surroundings.

8. What is the sign convention for work?

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9. A gas expands by a volume ΔV against a constant pressure P. What is

the work done by the system?

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10. Assertion : There is no change in internal energ in a cyclic process.

Reason : Internal energy is a state function.



11. Write the mathematical statement of first law of thermodynamics.

12. What happens to the internal energy of a system if work is done on

the system.

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13. What happens to the internal energy of a system if work is done by

the system?

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14. For the reaction, $N_2(g) + 3H_2(g)$ to $2NH_3(g)$, predict whether the

work is done by the system or on the system.

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15. Define internal energy of a system.



19. What is the value for ΔH for the given process,

 $NaOH(aq) + HCl(aq)
ightarrow NaCl(aq) + H_2O(l)$?



20. What do you understand by a spontaneous process ? Give two examples

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21. Which of the following processes are spontaneous and which are non-spontaneous ?

(i) Flow of air from high pressure to low pressure.

(ii) Formation of ice in a refrigerator.

(iii) Spreading of a drop of ink in water kept in a beaker.

(iv) Reverse osmosis.



25. If a system absorbs q amount of heat at temperature T, what would

be the change in the entropy of the system?





solid ?

33. Write the expression which gives the entropy of vapourisation of a

liquid.

Watch Video Solution
34. State and explain the second law of thermodynamics.
Watch Video Solution
35. Gibbs Free Energy
Watch Video Solution
36. What is the enthalpy of formation of the most stable form of an element in its standard state ?
Vatch Video Solution



38. What is the free energy criterion for a process to occur spontaneously?

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39. The free energy change $\Delta G=0$, when

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40. An endothermic process involves an increase in the entropy of the system. Predict the condition under which the process would be feasible.



41. An exothermic reaction involves a decrease in the entropy of the

system. Will the process be spontaneous ?

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Watch video Solution
42. How is standard free energy change related to equilibrium constant
?
watch video Solution
43. State the third law of thermodynamics.
Watch Video Colution
watch video Solution
44. What do you understand by the term thermochemistry ?
Watch Video Solution

45. Can chemical energy be transferred into electrical energy? If yes, give

an example.

Watch Video Solution

46. Assertion : ΔH for an exothermic reaction is negative nad for an endothermic reaction is positive.

Reason : Enthalpy is an extensive property.

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47. Why is it necessary to mention the physical state of substances in a

thermochemical equation ?

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48. Define heat of reaction.



51. State whether each of the following processes is exothermic or endothermic :

 $HCl(aq) + NaOH(aq)
ightarrow NaCl(aq) + H_2O(l), \Delta H = -57.1 kJ$

52. State whether the following processes is exothermic or endothermic

$$:H_2O(l)
ightarrow H_2O(s), \Delta H=~-~6.01kJ$$

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53. State whether each of the following processes is exothermic or endothermic : $H_2O(l) o H_2O(g), \Delta H= \ +\ 40.7 kJ.$

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54. Name the heat that is involved in the conversion of one allotropic

form into the other.



55. What would be the complications if Hess's law were not true?

56. What would be the bond formation energy of C-H bond if its bond

energy is $+416.18kJmol^{-1}$?



Short Answer Type Questions

1. Define thermodynamics. Describe the significance and limitations of

thermodynamics.

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2. Define the System.

3.	Define	State	of a	system.
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Watch Video Solution

4. Define State variables.



5. Explain with examples the various types of systems.

O Watch Video Solution

6. What do you understand by intensive and extensive properties of a

system ? Explain with examples.



7. In an adiabatic process

Watch Video Solution

8. Define the Cyclic process.



9. Define the Reversible process.

Watch Video Solution

10. Define heat and work and mention their sign conventions.

11.	State	and	explain	the	first	law	of	thermodynamics.	Derive	its
ma	thema	tical f	orm.							
_										_
	W at	tch Vi	deo Solu	tion						

12. Give the limitations of the first law of thermodynamics.

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13. Define internal energy of a system.

Watch Video Solution

14. Using the first law of thermodynamics, Show that $\Delta U = q_v$.



15. Define enthalpy and enthalpy change. Show that $\Delta H = q_p$.

Watch Video Solution

16. Define enthalpy. Show that the change in enthalpy at constant pressure for a reaction involving gases is given by the expression, $\Delta H = \Delta U + \Delta n_q$. RT.

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Watch Video Solution

17. Establish a relationship between ΔH and ΔU . Under what conditions is $\Delta H = \Delta U$?





22. Define enthalpy and enthalpy change. Show that $\Delta H = q_p$.

Watch Video Solution
23. What is the free energy criterion for a process to occur spontaneously?
Watch Video Solution
24. Explain the term 'entropy'.
Watch Video Solution

25. State giving reason whether the following reaction would involve an

increase, a decrease or no change in entropy.

 $4Fe(s)+3O_2(g)
ightarrow 2Fe_2O_3(s)$

26. What do you understand by a spontaneous process ? Give two examples

6	Watch	Video	So	lution
	Tracen	VIGCO	501	

27. What do you understand by the spontaneity of a process ? Discuss

the spontaneity of a process in terms of entropy and free energy.

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28. Can ΔH be regarded as the sole criterion to explain the spontaneity

of a process? If no, explain why?

29. With the help of at least two examples show that randomness increases in a spontaneous process.



D Watch Video Solution

32. What happens to the entropy when a gas undergoes expansion ?

Explain.



36. Show that the entropy change in an irreversible process is always

positive.

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37. Define 'entropy of fusion' and 'entropy of vapourisation and write expressions to represent them.

Watch Video Solution

38. State and explain the second law of thermodynamics.



39. Gibbs Free Energy

40. Derive the equation, $\Delta G = \Delta H - T \Delta S$.

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41. Give 2 points of difference between molarity and molality.

O Wate	ch Video	Soluti	on					
42. What	is the	free	energy	criterion	for a	process	to	occur
spontaneo	usly?	<u> </u>						

43. For the process $A+B
ightarrow C+D, \Delta G$ is positive. Comment on the

spontaneity of the process.
44. What are spontaneous processes ? Mention the conditions for a

reaction to be spontaneous at constant temperature and pressure.

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45. What is entropy ? State the effect of increased temperature on the entropy of a substance.

> Watch Video Solution

46. State the thermodynamic conditions for spontaneous occurrence of

a process.



47. ΔH and ΔS are positive for a chemical reaction. Under what conditions is the reaction expected to occur spontaneously?



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50. Comment on the spontaneity of a process when

 $\Delta H > 0, T\Delta S > 0 \, \, {
m and} \, \, T\Delta S < \Delta H$

51. Comment on the spontaneity of a process when

 $\Delta H > 0, T\Delta S < 0$

Watch Video Solution

52. Comment on the spontaneity of a process when

 $\Delta H > 0, T\Delta S > 0 \, \, {
m and} \, \, T\Delta S < \Delta H$

Watch Video Solution

53. Comment on the spontaneity of a process when

 $\Delta H > 0, T\Delta S > 0 \, \, {
m and} \, \, T\Delta S < \Delta H$



54. Discuss the effect of temperature on the spontaneity of a process.



59. What do you understand by exothermic and endothermic reactions ?

How are they related to the change in enthalpy?

Watch Video Solution
60. What do you understand by standard enthalpy of a reaction and how
is it represented ?
Watch Video Solution
61. Define heat of formation. How is it useful in the calculation of the
heat of a reaction ?
Watch Video Solution

62. Calculate the calorific value of sugar if its heat of combustion is $5645kJmol^{-1}$.



3. Derive an expression for the work done during an isothermal process.

Watch Video Solution									
4. State	and	explain	the	first	law	of	thermodynamics.	Derive	its
mathemat	tical f	orm.							

Watch Video Solution

5. What is internal energy and internal energy change? What is its significance ?



6. Establish a relationship between ΔH and ΔU . Under what conditions is $\Delta H = \Delta U$?



increase in the internal energy of the system, whereas that at constant

pressure is equal to the increase in the enthalpy of the system.





11. What do you understand by spontaneous and non spontaneous

processes ? What are the important features of a spontaneous process ?

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Watch Video Solution

12. What do you understand by the spontaneity of a process ? Discuss

the spontaneity of a process in terms of entropy and free energy.

> Watch Video Solution

13. What is entropy and how is it related to the spontaneity of a process?

14. Show that the entropy changes in a reversible isothermal process is

zero.

Watch Video Solution 15. Define the following and write expressions for calculating each of them. Entropy of fusion Watch Video Solution

16. Define the following and write expressions for calculating each of

them. Entropy of vapourisation.



17. Define the following and write expressions for calculating each of them. Entropy of sublimation.

Watch Video Solution
18. How would you calculate the entropy change in a chemical reaction ? How is it helpful in discussing the spontaneity of the reaction ?
Watch Video Solution

19. What is Gibbs free energy ? Derive the relation, $\Delta_G = \Delta H - T \Delta S$.

Discuss the free energy criterion for the spontaneity of a process.



20. What is the status of a process when (i) $\Delta G < 0$ (ii) $\Delta G = 0$ (iii)

 $\Delta G > 0$?



24. What do you understand by enthalpy and change in enthalpy? Why does a chemical reaction involve a change in enthalpy?

C	Watch	Video	So	lution

25. What are thermochemical equations and what is their significance in the study of chemical energetics ? State and explain the conventions used for writing a thermochemical equation.

Watch Video Solution

26. What is heat of reaction and on what factors does it depend?



27. Write shot notes on the Heat of formation.

28. Write shot notes on the Heat of combustion.

Watch Video Solution
29. Write shot notes on the Heat of solution.
Watch Video Solution
30. Write shot notes on the Heat of transition.
Watch Video Solution
31. Why is heat of neutralisation for a strong acid and strong base
constant ?

32. State and explain Hess's law of constant heat summation. Illustrate it

with examples. Discuss its important applications.

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Objective Multiple Choce Type Questions

1. Thermodynamics is concerned with

A. total energy of the system

B. energy changes in a system

C. rate of a chemical change

D. mass changes in nuclear reactions.

Answer: B

- 2. Thermodynamic equilibrium involves
 - A. chemical equilibrium
 - B. thermal equilibrium
 - C. mechanical equilibrium
 - D. all the three.

Answer: D

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3. During the isothermal expansion of an ideal gas, its

internal energy increases

enthalpy decreases

enthalpy remains unaffected

enthalpy reduces to zero.

A. internal energy increases

B. enthalpy decreases

C. enthalpy remains unaffected

D. enthalpy reduces to zero.

Answer: C

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4. Evaporation of water is:

a process in which heat is neither evolved nor absorbed

a process accompanied by chemical reaction

an exothermic change

an endothermic change.

A. a process in which heat is neither evolved nor absorbed

B. a process accompanied by chemical reaction

C. an exothermic change

D. an endothermic change.

Answer: D



5. Which of the following reactions is endothermic ? $CaCO_3(s)
ightarrow CaO(s) + CO_2(s)$ Fe(s) + S(s)
ightarrow FeS(s) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ $CH_4(q) + 2O_2(q) \rightarrow CO_{20}q) + 2H_2O(l).$ A. $CaCO_3(s)
ightarrow CaO(s) + CO_2(s)$ B. $Fe(s) + S(s) \rightarrow FeS(s)$ C. $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ D. $CH_4(g) + 2O_2(g) \rightarrow CO_{29}g) + 2H_2O(l)$.

Answer: A

6. For the reaction, $N_2[g]+3H_2[g] \Leftrightarrow 2NH_3[g], \Delta H=\dots$

A. $\Delta U - 2RT$

 $\mathrm{B.}\,\Delta U+2RT$

 $\mathsf{C}.\,\Delta U+RT$

D. $\Delta U - RT$.

Answer: A

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

 $2C_6H_6(l)+15O_2(g)
ightarrow 12CO_2(g)+6H_2O(l)$

at $25^{\,\circ}\,C$ in kJ is

A. + 7.43

B. + 3.72

 $\mathsf{C.}-7.43$

D. - 3.72

Answer: C

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8. A spontaneous change is one in which the system suffers:

an increase in internal energy

lowering in entropy

lowering in free energy

no energy change

A. an increase in internal energy

B. lowering in entropy

C. lowering in free energy

D. no energy change

Answer: C Watch Video Solution 9. In which of the following changes does entropy decrease ? A. Crystallisation of sucrose from solution B. Dissolving sucrose in water C. Melting of ice D. Vapourisation of camphor.

Answer: A

Watch Video Solution

10. For which reaction among the following, is ΔS maximum ?

A.
$$Ca(s)+rac{1}{2}O_2(g)
ightarrow CaO(s)$$

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

$$\mathsf{C}.\, C(s) + O_{29}g) o CO_2(g)$$

D.
$$N_2(g) + O_2(g) o 2NO(g)$$

Answer: B

Watch Video Solution

11. The free energy change for a reversible reaction at equilibrium is:

zero

small positive

small negative

large positive.

A. zero

B. small positive

C. small negative

D. large positive.

Answer: A

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A. ΔH is $+ve, \Delta S$ is also +ve

B. ΔH is -ve, ΔS is also - ve

C. ΔH is -ve, ΔS is + ve

D. ΔH is $+ve, \Delta S$ is -ve

Answer: D

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13. Which is an extensive property of the system?

Temperature

Volume

Refractive index

Viscosity.

A. Temperature

B. Volume

C. Refractive index

D. Viscosity.

Answer: B

Watch Video Solution

14. Which is not a state function of a thermodynamic system?

Internal energy (U)

Free energy (G)

Enthalpy (H)

Work (W).

A. Internal energy (U)

B. Free energy (G)

C. Enthalpy (H)

D. Work (W).

Answer: D

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15. Is the entropy of the universe constant ?

A. is increasing and tending towards a maximum value

B. is decreasing and tending towards zero

C. remains constant

D. decreasing and increasing with a periodic rate.

Answer: A

16. Decrease in free energy of a reacting system indicates:

an exothermic reaction

an endothermic reaction

a spontaneous reaction

a slow reaction.

A. an exothermic reaction

B. an endothermic reaction

C. a spontaneous reaction

D. a slow reaction.

Answer: C

Watch Video Solution

17. Gibbs free energy G, enthalpy H and entropy S are related as

A. G = H + TS

B. G = H - TS

C. G - TS = H

D. S = H - G .

Answer: B

Watch Video Solution

18. A system is provided 50 J of heat and work done on the system is 10 J.

The change in internal energy during the process is

A. 40 J

B. 60 J

C. 80 J

D. 50 J.

Answer: B

19. The entropy change for vapourisation of liquid water to steam $100^{\circ}C$ is $JK^{-1}mol^{-1}$. Given that heat of vapourisation is $40.8kJmol^{-1}$.

A. 109.38

B. 100.38

C. 110.38

D. 120.38

Answer: A

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20. The entropy change at a given temperature is expressed as:

 $q=T\Delta S$

 $\Delta S = q/\Delta T$

 $\Delta S = q - T$ S = q/TA. $q = T\Delta S$ B. $\Delta S = q/\Delta T$ C. $\Delta S = q - T$ D. S = q/T

Answer: A

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21. For an adiabatic process, which of the following is correct ?

$$P\Delta V = 0$$

 $q=\ +w$

 $\Delta E = q$

q=0

A. $P\Delta V=0$

B. q=~+~wC. $\Delta E=q$ D. q=0

Answer: D

Watch Video Solution

22. The amount of heat measured for a reaction in a bomb calorimeter

corresponds to

A. ΔG

 $\mathrm{B.}\,\Delta H$

 $\mathrm{C.}\,\Delta U$

D. $P\Delta V$.

Answer: C

23. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to a volume of 20 litres at $25^{\circ}C$ is

A. $2.303 imes 298 imes 0.082 \log_{10} 2$

B. $298 imes10^7 imes8.31 imes2.303\log_{10}2$

 $\text{C.}~2.303\times289\times0.082\log_{10}0.5$

D. $2.303 imes 298 imes 2 \log_{10} 2$.

Answer: B

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24. Which of the following values of heat of formation does indicate that

the product is least stable ?

- 94 kcal
- 231.5 kcal

+64.8 kcal.

+21.4 kcal

A. - 94 kcal

B. - 231.5 kcal

C. +21.4 kcal

D. +64.8 kcal.

Answer: D

Watch Video Solution

25. The heat of neutralisation is highest in

A. $NaOH + CH_3COOH$

 $\mathsf{B.}\,HCl+NaOH$

 $\mathsf{C.}\, NH_4OH + HCl$

 $\mathsf{D.}\,CH_3COOH+NH_4OH.$

Answer: B Watch Video Solution

26. The heat of neutralisation of NaOH and HCl is $57.3kJmol^{-1}$ then the amount of heat liberated if 2 moles each of NaOH and HCl are reacted is

A. 57.3 kJ mol

B. 114.6 kJ mol

C. 28.65 kJ mol

D. 215.2 kJ mol

Answer: B



27. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2

. At equilibrium, when the flask is heated at $100\,^\circ C$ the brown colour

deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH for this system is

A. negative

B. positive

C. zero

D. undefined

Answer: B

Watch Video Solution

28. The process of evaporation of a liquid is accompanied by:

increase in enthalpy

decrease in entropy

no change in free energy

increase in entropy.

A. increase in enthalpy

B. decrease in entropy

C. no change in free energy

D. increase in entropy.

Answer: D

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29. 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 :

A. 668 kJ

B. - 668 kJ

C. 112 kJ

D. - 112 kJ.

Answer: D

30. The standard enthalpy of formation of NH3 is -46.0 kJ mol^{-1} . If the enthalpy of formation of H_2 from its atoms is -436 kJ mol and that of N_2 is -712 kJ mol, the average bond enthalpy of N - H bond in NH_3 is

A. $-964kJmol^{-1}$

- $\mathsf{B.} + 352 k Jmol^{-1}$
- $C. + 1056 k Jmol^{-1}$
- D. $-1102kJmol^{-1}$

Answer: B

Watch Video Solution

31. The entropy change involved in the isothermal reversible expansion

of 2 moles of an ideal gas from a volume of 10 dm3 a volume of 100 dm3

at $27^{\,\circ}\,C$ is
A. $38.3 Jmol^{-1}k^{-1}$

- B. $35.8 Jmol^{-1}K^{-1}$
- C. $32.3 Jmol^{-1}K^{-1}$
- D. $42.3 Jmol^{-1}K^{-1}$

Answer: A

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32. In view of the signs of $\Delta_r G^\circ$ for the following reactions

 $PbO_2+Pb
ightarrow 2PbO, \Delta_r G^\circ\ < 0$

 $SnO_2+Sn
ightarrow 2SnO, \Delta_r G^\circ > 0$

Which oxidation states are more characteristic for lead and tin?

A. For lead + 4, for tin + 2

B. For lead + 2, for tin + 2

C. For lead + 4, for tin + 4

D. For lead + 2, for tin + 4.

Answer: D



33. The value of enthalpy change (ΔH) for the reaction

 $C_2H_5OH(l)+3O_2(g)
ightarrow 2CO_2(g)+3H_2O(l)$

at $27^{\circ}C$ is $-1366.5kJmol^{-1}$. The value of internal energy change for the above reaction at this temperature will be

 $\mathsf{A.}-1371.5kJ$

 $\mathrm{B.}-1369.0 kJ$

 ${\rm C.}-1364.0 kJ$

D. - 1361.5kJ

Answer: C

34. If the enthalpy change for the transition of liquid water to steam is $30kJmol^{-1}$ at $27^{\circ}C$ the entropy change for the process would be

A. $1.0 Jmol^{-1}K^{-1}$

B. $0.1 Jmol^{-1}K^{-1}$

C. $100 Jmol^{-1}K^{-1}$

D. $10Jmol^{-1}K^{-1}$.

Answer: C

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35. Which of the following is correct option for free expansion of an ideal gas under adiabatic condition?

A.
$$q
eq 0, \Delta T = 0, W = 0$$

B.
$$q=0, \Delta T=0, W=0$$

C.
$$q=0, \Delta T < 0, W
eq 0$$

D.
$$q=0,$$
 $\Delta T
eq 0,$ $W=0$

Answer: B

Watch Video Solution

36. Enthalpy change for the reaction,

 $4H(g)
ightarrow 2H_2(g)$ is -869.6 kJ

The dissociation energy of H - H bond is

 $\mathsf{A.}-869.6kJ$

 $\mathsf{B.}+434.8kJ$

 ${\rm C.+}217.4kJ$

 $\mathsf{D.}-434.8kJ$

Answer: B

37. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is ?

A. 10.52 cal/(mol K)

B. 21.04 cal/(mol K)

C. 5.260 cal/(mol K)

D. 0.526 cal/(mol K).

Answer: C

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38. Standard enthalpy of vapourisation $\Delta_{vap}H^-$ for water at $100^\circ C$ is $40.66 k Jmol^{-1}$. The internal energy of vapourisation of water at $100^\circ C$ (in kJ mol^{-1}) is (Assume water vapour to behave like an ideal gas).

B. -43.76

C. 43.76

D. + 40.66.

Answer: A

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39. In which of the following reactions, standard reaction entropy changes (ΔS) is positive and standard Gibbs energy change ('DeltaG`) decreases sharply with increasing temperature?

$$egin{aligned} &\mathsf{A.}\ C(ext{graphite}) + rac{1}{2}O_2(g) o CO(g) \ &\mathsf{B.}\ CO(g) + rac{1}{2}O_2(g) o CO_2(g) \ &\mathsf{C.}\ Mg(s) + rac{1}{2}O_2(g) o MgO(g) \ &\mathsf{D.}\ rac{1}{2}C(ext{graphite}) + rac{1}{2}O_2(g) o rac{1}{2}CO_2(g) \end{aligned}$$

Answer: A

40. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0mL at a constant temperature of $37.0^{\circ}C$. As it does so, it absorbs 208J of heat. The value of q and W for the process will be (R = 8.314J/molK, 1n7.5 = 2.01)

A. q = +208J, W = -208J

B.
$$q = -208J, W = -208J$$

C.
$$q=~-~208J, W=~+~208J$$

D.
$$q=~+~208J, W=~+~208J$$

Answer: A

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41. For complete combustion of ethanol, $C_2H_5OH(l)+3O_2(g)
ightarrow 2CO_2(g)+3H_2O(l),$ the amount of heat

produced as measured in bomb calorimeter , is $1364.47kJmol^{-1}$ at $25^{0}C$. Assuming ideality the Enthalpy of combustion, $\Delta_{C}H$, for the reaction will be: $(R = 8.314kJmol^{-})$.

A. $-1366.95 k Jmol^{-1}$

B. $-1361.95 k Jmol^{-1}$

C. $-1460.50 k Jmol^{-1}$

D. $-1350.50 k Jmol^{-1}$

Answer: A

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42. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be

A. 1136.25 J

 $\mathrm{B.}-500J$

C. -505 J

D. +505 J

Answer: C

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43. For a given reaction, $\Delta H = 35.5 k Jmol^{-1}$ and $\Delta S = 83.6 J K^{-1} mol^{-1}$. The reaction is spontaneous at (Assume that ΔH and ΔS do not vary with temperature)

A. T lt 425 K

B. Tgt 425 K

C. All temperatures

D. Tgt 298 K

Answer: B

$$egin{aligned} & extsf{44. Given } C_{(extsf{graphite})} + O_2(g) o CO_2(g), \ & \Delta_r H^0 = -393.5 kJ \quad mol^{-1} \ & H_2(g) = +rac{1}{2}O_2(g) o H_2O(1), \ & \Delta_r H^0 = -285.8 \ extsf{kJ} \quad mol^{-1} \ & CO_2(g) + 2H_2O(1) o CH_4(g) + 2O_2(g), \ & \Delta_r H^0 = +890.3 kJ \quad mol^{-1} \end{aligned}$$

Based on the above thermochemical equations, the value of $\Delta_r H^0$ at at 298 K for the reaction

 ${C}_{(\,{
m graphite}\,)}\,+2H_2(g)
ightarrow CH_4(g)$ will be:

A. $-74.8 k Jmol^{-1}$

 $B. -144.0 k Jmol^{-1}$

 $\mathsf{C.}+74.8 kJmol^{-1}$

D. $+144.0 k Jmol^{-1}$

Answer: A

45. ΔU is equal to

A. adiabatic work

B. isothermal work

C. isochoric work

D. isobaric work

Answer: A



46. The bond dissociation energies of X_2 , Y_2 and XY are in the ratio of $1: 0.5: 1. \Delta H$ for the formation of XY is -200 kJ mol^(-1) . *Thebonddissociatione* $\neq rgyofX_2$ ` will be

A. $200kJmol^{-1}$

B. $100kJmol^{-1}$

C. $800kJmol^{-1}$

D. $400kJmol^{-1}$

Answer: C

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47. The combustion of benzene(/) gives $CO_2(g)$ and $H_2O(l)$ Given that heat of combustion of benzene at constant volume is $-3263.9kJmol^{-1}$ at $25^{\circ}C$, heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be

 $\left(R = 8.314 J K^{-1} mol^{-1}
ight)$

A. 4152.6

 $\mathsf{B.}-452.46$

C. 3260

D. - 3267.6

Answer: D



48. For the cell reaction

 $2Fe^{3+}(aq)+2l^{-1}(aq)
ightarrow 2Fe^{2+}(aq)+I_2(aq)$

 $E_{
m cell}^{\,\Theta}=0.24V$ at 298 K. The standard Gibbs energy $\left(\Delta_r G^{\,\Theta}
ight)$ of the cell reaction is

[Given that Faraday constnat $F = 96500 Cmol^{-1}$]

A. $46.32 k Jmol^{-1}$

B. $23.16 k Jmol^{-1}$

 $\mathsf{C.}-46.32 kJmol^{-1}$

 $\mathsf{D}.-23.16 kJmol^{-1}$

Answer: C

49. Under isothermal condition, a gas at 300 K expands from 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is (Given that 1 L bar = 100 J)

A. 25 J

B. 30 J

C. -30 J

D. 5 kJ.

Answer: C

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50. In which case change in entropy is negative?

A. Sublimation of solid to gas

 ${\tt B.}\, 2H(g) \to H_2(g)$

C. Evaporation of water

D. Expansion of a gas at constant temperature.

Answer: B

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51. For a cell involving one electron $E_{cell}^0 = 0.59V$ and 298K, the equilibrium constant for the cell reaction is: [Given that $\frac{2.303RT}{F} = 0.059V$ at T = 298K] A. 1.0×10^5 B. 1.0×10^{10} C. 1.0×10^{30} D. 1.0×10^2

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Answer: B

52. The INCORRECT match in the following is

A.
$$\Delta G^{\,\circ}\,=0,\,K=1$$

B. $\Delta G^\circ \, < 0, \, K < 1$

C.
$$\Delta G^\circ > 0, K < 1$$

D. $\Delta G^{\,\circ}\,< 0, K>1$

Answer: B

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53. 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 ΔU (in kj) is

A. 12

B.-8

C. 8

D. - 12

Answer: C



54. Consider the given plot of enthalpy of the following reaction between A and B. $A + B \rightarrow C + D$. Identify the incorrect statement.



A. C is the thermodynamically stable product.

B. Formation of A and B from C has highest enthalpy of activation.

C. Activation enthalpy to form C is 5 kJ mor less than that to form D.

D. D is kinetically stable product.

Answer: C



55. The standard Gibbs energy for the given cell reaction in kJ mol^{-1} at 298 K is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s), E^{\circ} = 2V$ at 298K

(Faraday's constant, $F=96000Cmol^{-1}$)

A. - 192

B. 192

C. -384

D. 384

Answer: C

56. Among the following, the set of parameters that represents path functions is

(A) q + w (B) q (C) w (D) H - TS

A. (A), (B) and (C)

B. (B) and (C)

C. (A) and (D)

D. (B), (C) and (D).

Answer: B

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57. 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)

A. Adiabatic process : $\Delta U = -w$

- B. Cyclic process : $q=\ -w$
- C. Isothermal process : q = -w
- D. Isochoric process : $\Delta U = q$.

Answer: A

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58. For silver, $C_P(JK^{-1}\text{mol}^{-1}) = 23 + 0.01T$. If the temperature (T) of 3 moles of silver is raised from 300K to 1000K at 1 atm pressure, the value of ΔH will be close to :

A. 13 kJ

B. 16 kJ

C. 62 kJ

D. 21 kJ

Answer: C



59. 5 moles of an ideal gas at 100 K are allowed to undergo reversible compression till its temperature becomes 200 K. If $C_V = 28JK^{-1}mol^{-1}$, calculate ΔU and ΔpV .

A.
$$\Delta U = 14J, \Delta(pV) = 0.8J$$

B.
$$\Delta U = 14kJ, \Delta(pV) = 4kJ$$

C.
$$\Delta U = 14kJ, \Delta(pV) = 18J$$

D.
$$\Delta U=2.8kJ,$$
 $\Delta(pV)=0.8kJ.$

Answer: B

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True Or False Type Questions

1. Thermodynamics mainly deals with

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2. An animal is an open system.
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3. Volume is an intensive property.

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4. Which of the following are not state functions ?

Temperature, entropy, heat, work, enthalpy, internal energy.





9. $\Delta E = E_{ m initial\,state} - E_{ m final\,state}$



 $Zn(s)+2HCl(aq)
ightarrow ZnCl_2(aq)+H_2(g), \Delta H$ is equal to $\Delta E.$

13. Decomposition of $CaCO_3$ is a reversible reaction when carried out in

an open kiln.

Watch Video Solution 14. State True/False All spontaneous process proceed in one direction only. Watch Video Solution **15.** The units of ΔS are $JK^{-1}mol^{-1}$. Watch Video Solution 16. The absolute entropy of a liquid is less than of the solid.

17. Is the entropy of the universe constant ?
Watch Video Solution
18. A process is non-spontaneous when $\Delta S_{ m total} < 0.$
Watch Video Solution
19. For an irreversible process, $\Delta S > 0$.
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20. Heat can be converted completely into equivalent amount of work without producing changes elsewhere.



21. A chemical process always proceeds in the direction in which the

Gibbs free energy of the system decreases.



1. Thermodynamics mainly deals with

Watch Video Solution	
2. A closed system is that which	
Watch Video Solution	

3. A system is said to be in equilibrium when the system and the surroundings are at the same temperature.



4. When the work is done by the system, w is taken as



9. A spontaneous process is also called a process.

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10. Dissolution of sugar in water is accompanied by of entropy of the

system.

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11. A spontaneous process is an process and occurs in direction

only.

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12. The force responsible for the spontaneity of a reaction is called

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13. The total entropy change (\Delta S_{\rm total}) for the system and surrounding of a spontaneous process is given by 
Watch Video Solution
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14. If $\Delta S_{
m total}$ is positive the process is and occurs in the as mentioned. The reverse process is

Watch Video Solution

15. Whenever a spontaneous process takes place, it is accompanied by

an increase in the total of the



16. When $\Delta G=0$, the process is

17. When ΔH is ngative nad $T\Delta S$ is positive, the process isat all......

19. The greater the free energy change, the greater is the amount of

work that can be obtained from the process.



20. At absolute zero, the entropy of a pure crystal is zero. This is

1. The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero.

The volume occupied by the molecules of an ideal gas is zero.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: B

2. Assertion : The total energy of the universe is constant.

Reason : When a quantity of some form of energy disappears, an exactly equivalent amount of some other form of energy is produced.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: A



3. Assertion : The heat of a reaction does not depend upon the

temperature at which reaction is carried out.

Reason : Temperature is a state function.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: D

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4. Assertion : The heat of neutralisation for a strong acid and a weak base is always equal to -57.1 kJ.

Reason : One gram equivalent of a strong acid always neutralises one

gram equivalent of a weak base.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: D

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5. Assertion : The bond energy and bond formation energy of a particular bond are equal in magnitude but opposite in sign.Reason : The process of bond formation requires absorption of energy

but the process of breaking of bond involves liberation of energy.
A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: C

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6. Assertion : The sun is the ultimate source of all types of energies and sustains life on earth.

Reason : The solar energy gets converted into all types of energies present on the earth.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: A

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7. Assertion : A perpetual machine can produce work continuously without consuming energy.

Reason : Energy can be converted from one form to another.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: D

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8. Assertion : Burning of coal is a spontaneous process.

Reason : Coal when ignited burns of its own accord without any outside assistance.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: A

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9. Assertion : All spontaneous processes are thermodynamically irreversible.

Reason : In a reversible isothermal process, there is no net change in entropy.

A. If both Assertion and Reason are CORRECT and Reason is the

CORRECT explanation of the Assertion.

B. If both Assertion and Reason are CORRECT but Reason is not the

CORRECT explanation of the Assertion.

C. If Assertion is CORRECT but Reason is INCORRECT.

D. If Assertion is INCORRECT but Reason is CORRECT.

Answer: B



Numberical Problems

1. Calculate the free energy change when one mole of sodium chloride is dissolved in water at 298 K. (Given : Lattice energy of NaCl $= -777.8kJmol^{-1}$, Hydration energy of NaCl $= 774.1kJmol^{-1}$ and ΔS at $298K = 0.043kJmol^{-1}$.

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2. Calculate the value of equilibrium constant, K for the following reaction at 400 K.

 $2NOCl(g) \Leftrightarrow 2NO(g) + Cl_2(g)$

$$\Delta H^{\,\circ}\,=\,80.0kJmol^{\,-1},\,\Delta S^{\,\circ}\,=\,120KJ^{\,-1}mol^{\,-1}$$
 at 400 K, R = $8.31JK^{\,-1}mol^{\,-1}.$

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3. Calculate the standard free energy change for the following reaction at $27^{\circ}C$. $H_2(g) + I_2(g) \rightarrow 2HI(g), \Delta H^{\circ} = +51.9kJ$ [Given : $\Delta S_{H_2}^{\circ} = 130.6JK^{-1}mol^{-1}$ $\Delta S_{I_2}^{\circ} = 116.7JK^{-1}mol^{-1}$ $\Delta S_{HI}^{\circ} = 206.3JK^{-1}mol^{-1}$].

Predict whether the reaction is feasible at 27°C or not.

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4. Using the data given below, calculate the value of equilibrium constant for the reaction

 $3HC\equiv CH(g) \Leftrightarrow {C_6H_6(g)} {
m benzene}$

at 298 K, assuming ideal behaviour.

$$\Delta_f G^\circ HC \equiv CH(g) = 2.09 imes 10^5 Jmol^{-1}$$
,

$$\Delta_{f}G^{\,\circ}C_{6}H_{6}(g)=1.24 imes 10^{5} Jmol^{-1}$$

$$R = 8.314 J K^{-1} mol^{-1}$$

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5. Give the reaction for preparing benzene.

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6. A gas expands from $3dm^3$ to $5dm^3$ against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10 moles of water at temperature 290 K. Calculate the final temperature of water. Specific heat of water = $4.184JK^{-1}g^{-1}$.

7. The enthalpy change involved in the oxidation of glucose is $-2880kJmol^{-1}$. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometre, what is the maximum distance that a person will be able to walk eating 120 g of glucose ?

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8. 10 g of argon is compressed isothermally and reversibly at a temperature of $27^{\circ}C$ from 10 L to 5L. Calculate , w, ΔE and ΔH for the process. $R = 2.0 cal K^{-1} mol^{-1}$, $\log 2 = 0.30$, At. Wt. of argon = 40.

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9. Using data (all values are in kilocalorie per mole at $25^{\circ}C$) given below, calculate the bond energy of C-C and C-H bonds. ΔH^{Θ} combustion of ethane = -372.0 ΔH^{Θ} combustion of propane = -530.0 ΔH^{Θ} for C(garphite) $\rightarrow C(g) = +172.0$ Bond enegry of H - H bond = +104.0 $\Delta_f H^{\Theta} of H_2 O(l) = -68.0$ $\Delta_f H^{\Theta} of CO_2(g) = -94.0$

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10. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid the storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is $44kJmol^{-1}$.

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11. The standard enthalpy of formation of H 2 O(I) and Fe 2 O 3 (s) are respectively -286 kJ mol -1 and -824 kJ mol -1. What is the standard



 $C \equiv C$ bond energy assuming that the bond energy of C-H is 93.6 kcal.

Heat of atomisation of carbon and hydrogen are 150 and 51.5 kcal respectively.



14. If a man submits to a diet of 9500 kJ per day and expands energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg ? (Ignore water loss for this problem.)

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15.
$$C(s)+O_2(g)
ightarrow CO_2(g)+394kJ$$
 $C(s)+rac{1}{2}O_2(g)
ightarrow CO+111kJ$

In an oven using coal (assume the coal is 80% C in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% of carbon is converted to CO. Find out the heat generated when 10 kg of coal is burnt in this fashion.

16.
$$C(s)+O_2(g)
ightarrow CO_2(g)+394kJ$$
 $C(s)+rac{1}{2}O_2(g)
ightarrow CO+111kJ$

Calculate the heat generated if efficiency of oven is 10.8% and a fully efficient oven converts all the carbon to CO_2

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17.
$$C(s)+O_2(g)
ightarrow CO_2(g)+394kJ$$
 $C(s)+rac{1}{2}O_2(g)
ightarrow CO+111kJ$

Calculate the percentage loss in heating value for the inefficient oven.

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18. Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane. The heat of combustion of methane to CO_2 and water (gas) is given by

$$CH_4(g) + 2O_2(g) o CO_2(g) + 2H_2O(g) + 809kJ.$$

How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20,000 kJ of energy per day to meet all its needs and that the methane content in gobar gas is 80% by weight?

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Ncert Text Book Exercises

- 1. Choose the correct answer.
- A thermodynamic state function is a quantity.
- (a) used to determine heat changes.
- (b) whose value is independent of path.
- (c) used to determine pressure volume work.
- (d) whose value depends on temperature only.
 - A. used to determine heat changes
 - B. whose value is independent of path

C. used to determine pressure volume work

D. whose value depends on temperature only.

Answer: B

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2. For the process to occur under adiabatic conditions, the correct condition is

A. $\Delta T=0$

B. $\Delta p=0$

 $\mathsf{C.}\,\Delta q=0$

 $\mathsf{D}.\,w=0$

Answer: C

3. The enthalpies of all elements in their standard states are

A. unity

B. zero

 $\mathsf{C}. \ < 0$

D. different for each element.

Answer: B

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4. $\Delta U^{\,\circ}\,$ of combustion of methane is $-XkJmol^{-1}.$ The value of $\Delta H^{\,\circ}$

is

A. $=\Delta U^{\,\circ}$

B. $>\Delta U^{\,\circ}$

C. $<\Delta U^{\,\circ}$

 $\mathsf{D.} = 0$

Answer: C



5. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, $-890.3kJmol^{1} - 393.5kJmol^{-1}$, and $-285.8kJmol^{-1}$ espectively. Enthalpy of formation of $CH_4(g)$ will be

A.
$$-74.9kJmol^{-1}$$

B.
$$-52.27kJmol^{-1}$$

 $C. + 74.8 k Jmol^{-1}$

D. $+52.26 k Jmol^{-1}$

Answer: A

6. A reaction A + B
ightarrow C + D + q is found to have a positive entropy

change. The reaction will be

A. possible at high temperature

B. possible only at low temperature

C. not possible at any temperature

D. possible at any temperature.

Answer: D

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7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy of the process?

8. The reaction of cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7kJmol^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K. $NH_2CH(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(1)$

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9. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from $35^{\circ}C$ to $55^{\circ}C$. Molar heat capacity of Al is 24 J $mol^{-1}K^{-1}$.

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10. The enthalpy change on freezing of 1 mol of water at 5° C to ice at

 -5° C is :

(Given $\Delta_{ ext{fus}} H = 6 K J ext{mol}^{-1} ext{ at } 0^\circ C,$



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12. Enthalpies of formation of CO(g). $CO_2(g)$ and N_2O_4 are -110, -393, 81 and $9.7kJmol^{-1}$ respectively. Find the value of $\Delta_r H$ for the reaction :

$$N_2O_4(g)+3CO(g)
ightarrow N_2O(g)+3Co_2(g)$$

13. Given

$$N_2(g) + 3H_2(g) o 2NH_3(g), \Delta_r H^{\, \Theta} \, = \, - \, 92.4 k Jmol^{-1}$$

What is the standard enthalpy of formation of NH_3 gas?

14. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the

following data

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15. Calculate the enthalpy change for the process

 $CCI_4(g)
ightarrow C(g) + 4CI(g)$

and calculate bond enthalpy of C - Cl in $CCI_4(g)$.



16. For an isolated system, $\Delta U=0$, what will be ΔS ?

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17. For the reaction at 298 K,

 $2A + B \rightarrow C$

 $\Delta H = 400 K J mol^{-1}$ and $\Delta S = 0.2 k J K^{-1} mol^{-1}$

At what temperature will the reaction become spontaneous considering

 ΔH and ΔS o be constant over the temperature range.

18. For the reaction, $2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?



19. For the reaction

2A(g) + B(g)
ightarrow 2D(g)

 $\Delta U^{ heta}=~-~10.55 KJ$ and $\Delta S^{ heta}=~-~44.1 JK^{-1}$

Calculate $\Delta G^{\,\Theta}$ for the reaction, and predict whether the reaction may

occur spontaneously

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20. The equilibrium constant for a reaction is 10. What will be the value

of ΔG° ? $R=8.314JK^{-1}mol^{-1}, T=300K.$

21. Comment on the thermodynamic stability of $NO_{(g)}$, given

$$egin{array}{lll} rac{1}{2}N_2(g)+rac{1}{2}O_2(g) o NO(g) &: & \Delta_r H^ heta=90kJmol^{-1}\ NO(g)+rac{1}{2}O_2(g) o NO_2(g) &: & \Delta_r H^ heta=-74kJmol^{-1} \end{array}$$

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22. Calculate the entropy change in surroundings when 1.00 mole of $H_2O(l)$ is formed under standard conditions.

 $\Delta_{f} H^{\,\circ} = \,-\,286 k Jmol^{-1}$