

#### **CHEMISTRY**

### **JEE (MAIN AND ADVANCED) CHEMISTRY**

#### **CHEMICAL THERMODYANMICS**

Problem

1. A closed steel Mask contains hot tea. What type of system is this?



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2. Does the temperature remain constant in an adiabatic process?



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3. 10 grams of steam at  $100^{\circ}$  C is mixed with 50 gm of ice at  $0^{\circ}$  C then final temperture is



**4.** A chamber contains  $77gofCO_2$ . The chamber was divided into three compartments X, Y and Z as shown below. Suggest the relation between the internal energies of the gas in the three compartments X, Y and Z.

 $Z44qCO_2$ 



 $y22qCO_2$ 

 $X~11qCO_2$ 

**5.** What are the values of w and  $\Delta E$ , when a system absorbs 250J of heat by expanding from 1 lit to 10 lit against 0.5 atm pressure and at constant temperature.



**6.** A system absorbs 10kJ of heat at constant volume and its temperature rises from  $27^{0}C$  to  $37^{0}C$ . The DE of reaction is



**7.** From the observations given below, suggest the relation between X, Y and Z

Experiment	Heat supplied	Work done	ΔΕ
1	100J Supplied to the system	200J done by the system	X Joules
II	200J Supplied to the system	200J done on the system	Y Joules
III	400J lost to the system	100J done by the system	Z Joules



8. What is Mayer's relation?



**9.**  $N_{2\,(\,g\,)}\,+O_{2\,(\,g\,)}\,+180.6kJ
ightarrow\,2NO_{\,(\,g\,)}$  , calculate (a) heat of reaction,

(b) heat of formation of nitric oxide and (c) heat required to form one litre of nitric oxide at  $25\,^{\circ}\,C$ .



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**10.**  $\Delta H^0$  for a reaction  $F_2+2HCl o 2HF+Cl_2$  is given as  $-352.8kJ.~\Delta H^0_f$  for HF is  $-268.3KJmol^{-1}$ , then  $\Delta H^0_f$  of HCl would be



**11.** 
$$H_{2\,(\,g\,)}\,+\,rac{1}{2}O_{2\,(\,g\,)}\, o H_{2}O_{\,(\,l\,)}\,, \Delta H=\,-\,286.2KJ$$

$$H_2O_{\,(\,l\,)}\, o H_{\,(\,ag)}^{\,+} + OH_{\,(\,ag)}^{\,-}, \Delta H = \,+\,57.3KJ$$

Enthalpy of ionization  $OH^-$  in aqueons solution is



12. 4.184g of benzoic acid was burnt in bomb calorimeter. The rise in the temperature is  $10^{\circ}$ . The heat capacity of calorimeter and its contents is

 $2.644kcalK^{-1}$ . Calculate the heat of combustion of benzoic acid.



**13.**  $H_2SO_4(aq)+2NaOH_{(aq)} o Na_2SO_4(aq)+2H_2O_{(l)}$  . Suggest the hest of this reaction.



14.

 $HCN_{(aq)} + NaOH_{(aq)} 
ightarrow NaCN_{(aq)} + H_2O_{(1)}, \Delta H = -12.13KJ$ 

Calculate heat of ionisation of HCN.



**15.** For the reaction  $2SO_2(g)+O_2(g) o 2SO_3(g)$ . What is the realation between  $\Delta H$  and  $\Delta E$  ?



**16.** One mole of solite AB dissolved in 20 moles of water absorbed 15.9 KJ of heat. When one male of same se is dissolved in 250 moles of water

18.58KJ of heat is absorbed. Calculate the enthalpy of dilution



**17.**  $\Delta H$  for the formation of XY is  $-200kJmol^{-1}$ . The bond enthalpies of  $X_2,Y_2,~$  and XY are in the ratio 1:0.5:1. Then determine the bond enthalpies.



**18.** Heats of combustion of garphite carbon and carbon monoxide are respectively -393.5 KJ  $mol^{-1}$  and  $-110.5 mol^{-1}$ . Then determine the bond enthalpies.



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**19.** Heats of combustion diamond carbon and garphite carbon are respectively -395.4 KJ  $mol^{-1}$  and -393.5 KJ  $mol^{-1}$ . Calculate the heat of transition of dimand carbon into garphite carbon.



**20.** Heats of combustion of benzene, carbon and hydrogen are  $-782,\ -94,\ -68kcalmol^{-1} \ {\rm respectively.} \ {\rm Calculate\ heat\ of\ formation\ of\ benzene.}$ 



**21.** The bond enthalpies of D-D and O-O and D-O are respectively +440 ,+498 and +491.5KJ  $m mol^{-1}$  calculation  $\Delta H$  for the reaction  $D_2(g)+rac{1}{2}O_2(g) o D_2O(l)$ 



22. The heat of formation of crystalline sodium chloride is  $-410kJmol^{-1}$ . The heat of sublimation of sodium metal is  $180.8kJmol^{-1}$ . The heat of dissociation of chlorine gas into atoms is  $242.7kJmol^{-1}$ . The ionisation energy of Na and electron affinity of Cl are 493.7kJ and -368.2kJ respectively. Calculate the lattice energy of NaCl.



**23.** The standard molar heat for formation of ethane, carbondioxide and water are respectively, -21.1,-94.1 and -68.3 Kacal  $\mathrm{mol}^{-1}$ . What is the standard molar heat of combustion of ethane ?



**24.** The entropy change for vaporisation of a liquid is  $109.3JK^{-1}mol^{-1}$ .

The molar heat of vaporisation of that liquid is  $40.77kJmol^{-1}$ . Calculate the boiling point of that liquid.



following.

25. Based on entropy Change predict a spontaneous reaction among the

$$(A)\!:\!(NH_4)_2CO_3(s) o 2NH_3(g)+CO_2(g)+H_2O(l) \ \ ext{and} \ \ (B)\!:\!NH_3(g)$$

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**26.** Latent heat of fusion of ice is  $6kJmol^{-1}$ . Calculate the entropy change in the fusion of ice.



**27.** The vapour pressures of benzene at 303k and 333k are respectively  $1.53 \times 10^4$  and  $5.2 \times 10^4 Nm^{-2}$  Calculate the latent heat of evaporation of benzene over this temperature.



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**28.**  $Zn_{(s)}+Fe_{aq}^{2+}\Leftrightarrow Zn_{aq}^{2+}+Fe_{(s)}$  . The vale of  $K_c$  for this reaction is `10^(23). Calculate the standard free energy change.



**29.** The reaction,  $H_{2(g)}+\frac{1}{2}O_{2(g)}\to H_2O_{(l)}$ , is spontaneous. The  $\Delta S^\circ=-163.1Jmol^{-1}K^{-1}$ . The absolute entropies of  $H_{2(g)}$  and  $O_{2(g)}$  are  $130.6JK^{-1}mol^{-1}$  and  $205JK^{-1}mol^{-1}$  respectively. Calculate the absolute entropy of water.



**30.** How entropy change in the following process.

(a) boiling of egg , (b) stretching of rubber: (c ) Formation of micells

$$\mathsf{(d)}CH_3COOH_{(\mathit{aq})} \Leftrightarrow CH_3COO_{(\mathit{aq})}^- + H_{(\mathit{aq})}^+.$$

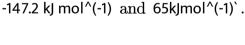


**31.** The formula  $\Delta S = \frac{q_{rev}}{T}$  can be isothermal irreversble expansion or not ?

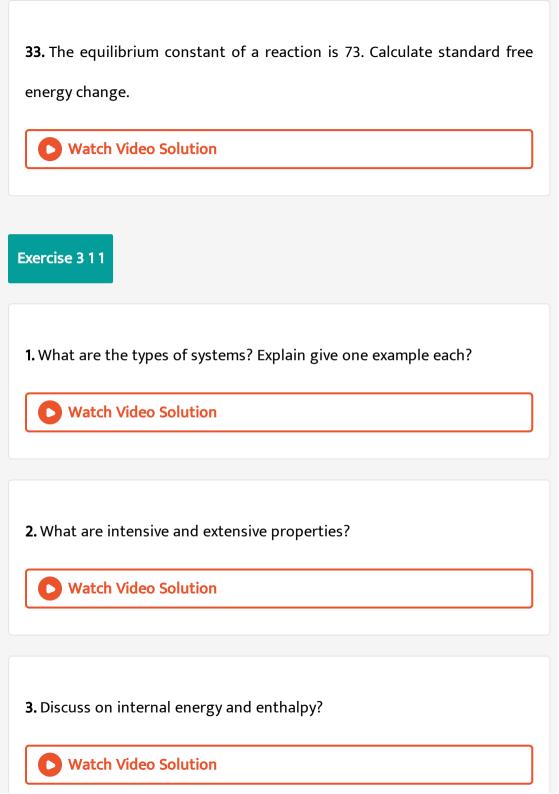


**32.** Calculate  $DetlaG^{\circ}$  for the following reaction,  $Zn \hookrightarrow \bot Cu^{2+} \to Zn^{2+} \bot Cu \hookrightarrow \Delta G^{\circ}$  of  $Zn^{2+}$  and  $Cu^{+2}$  is

 $Zn_{(s)} + Cu_{(aq)}^{2+} o Zn_{(aq)}^{2+} + Cu_{(s)}$  .  $\Delta G_f^{\circ}$  of  $Zn_{(aq)}^{2+}$  and  $Cu_{(aq)}^{+2}is$ 







<b>4.</b> State the first law of thermodynamics.	



- **5.** Define heat capacity. What are  $C_p \,\, ext{ and } \,\, C_v$ ? Show that  $C_p C_v = R$ .
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**6.** Differentiate exothermic and endothermic reactions.



7. What is a thermochemical equation? Write its significance.



**8.** An ideal gas expands from  $500cm^3$  to  $700cm^3$  against 1 atm pressure, by absorbing 2J of energy. Calculate change in internal energy of the ideal gas.



# Exercise 3 1 2

1. What is heat of a reaction? Discuss the factors on which it is dependent.



**2.** Define heat of formation. Write suitable examples.



3. What is combustion?



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4. Define heat of neutralisation. Write the basic equation. Why the heat liberated by the neutralisation of a weak acid is less than  $57.3kJmol^{-1}$ ?



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**5.** Heat of neutralisation of  $CH_3COOH_{(aq)}$  with  $NaOH_{(aq)}$  is - 55.2kJ.

What is heat of ionisation of  $CH_3COOH$ ?



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6. Heats of ionisation of acetic acid and ammonium hydroxide are  $xkJmol^{-1}$  and  $ykJmol^{-1}$ . Heat of neutralisation of HCl and NaOH is

 $zkJmol^{-1}$ . Calculate the heat when acetic acid is neutralised with ammonium hydroxide.  $\left(z-(x+y)kJmol^{-1}\right)$ 



7. State and explain Hess law. Write its important applications



**8.** 500mL of IM HCl and 500mL of 1M NaOH are mixed in Dewar flask. Then rise in temperature is  $T_1$ . In another experiment 1000mL1MHCl and 1000mLof1MNaOH are mixed in Dewar flask. Then rise in temperature is  $T_2$ . What is the relation between  $T_1$  and  $T_2$ ?



**9.** Heats of atomisation of chlorine and hydrogen are  $243kJmol^{-1}$  and  $435kJmol^{-1}$  respectively. Heat of formation of HCl is

 $-92kJmol^{\,-1}$ . Calculate the bond energy of HCL.



**10.** Define heat of bond dissociation. How are bond enthalpies useful in the determination of heat of reaction ?



**11.** Heats of formation of  $CH_3COOH(l), CO_2(g)$  and  $H_2O(l)$  are respectively -487, -394 and -286 kJ  $mol^{-1}$ . Calculate the heat of combustion of acetic acid.



12. When 2.4g of carbon reacted with X g of oxygen to form CO and  $CO_2$ , 50.4 kJ of heat was released and no reactant is left over. Standard heats of

formation of carbon monoxide and carbon- dioxide are -110.5 kJ  $mol^{-1}$  and -393.5 kJ  $mol^{-1}$  respectively, Calculate X.

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1. Discuss the following:

- (a) entropy and (b) entropy change.
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- **2.** Explain whether a reaction occurs on its own, by considering the entropy change of the reaction.
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**3.** Do all exothermic reactions occur spontaneously?



**4.** The absolute entropies of  $H_{2(g)}$ ,  $O_{2(g)}$  and  $H_2O_{(l)}$  are respectively 130.6, 205.1 and  $69.9JK-mol^{-1}$ . Calculate the value of  $\Delta S$  for the formation of one mole liquid water.



Exercise 3 1 4

1. Define Gibbs energy. How is it related to enthalpy and entropy?



2. What are the criteria for the spontaneity of chemical reaction?



3. How are absolute entropy values of substances determined?



**4.** At 300K, heat of dissociation of lime stone is  $+180kJmol^{-1}$ . Entropies of  $CaCO_3, CaO$  and  $Co_2$  are respectively

 $93,\,39\,$  and  $\,213 Jmol^{\,-1}K^{\,-1}.\,$  Calculate  $\Delta S_{
m total}$ 



**5.**  $4Fe(s)+3O_{2\,(g)}\to 2Fe_2O_3(g).$  The value of  $\Delta S$  is  $-550JK^{-1}$  and the value of DH is -1650kJ at 298 K. Does the process is spontaneous or not?



**6.** For the equilibrium system,  $2NOCI_{(g)}\Leftrightarrow 2NO_{(g)}+Cl_2(g)$  the value of  $\Delta G^\circ$  is 28.4 KJ.Calculate the value of equilibrium constant,  $K_e$ .



**7.** The e.m.f. of the cell reaction

 $Zn_{(s)}+Cu_{(aq)}^{+2} o Zn_{(aq)}^{+2}+Cu_{(s)}$  is 1.1 V. Calculate the free energy of the cell reaction.



## **Questions For Descriptive Answers**

**1.** How does heat of neutralisation value change with the chemical nature of acid and base?



**2.** How does entropy changes with the transformation at different temperature?

**3.** At 400K, 5 moles of an ideal gas expands isothermally and reversibly from  $10dm^3$  to  $20dm^3$ . Calculate the work done by the gas.



**4.** The molar heat capacity at constant volume of a system is 12.41J.  $mol^{-1}$ . In an adiabatic expansion the temperature of one mole of that gas falls from 298K to 288K. Calculate the work done by the gas.



**5.** Enthalpy of ammonia and water are  $-46.19KJ.\ mol^{-1}$  and  $-285.9KJ.\ mol^{-1}.$  Calculate AH for the reaction,  $4NH_3(g)+3O_2(g)\to 2N_2(g)+6H_2O(l).$ 



6.

 $H_2+Cl_2
ightarrow 2HCl, \Delta H_1, N_2+3H_2
ightarrow 2NH_3, \Delta H_2 \;\; ext{and}\;\;\;\; NH_3+3Cl_2 \;\; .$ 

Then calculate the heat of formation of nitrogen trichloride.



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**7.** The heat of combustion a sugar is  $-790 KJmol^{-1}$ . A person requires 2370KJ of energy for his daily activities and he consumed 540 g of sugar to meet his activities. Calculate the molecular weight of the given sugar.



**8.** Given that bond energies of N=N,H-H and N-H bonds as 945, 436 and 391 kJ/ mol respectively ,the enthalpy of the reaction

$$N_2(g) + 3H_2(g) + \ 
ightarrow \ 2NH_3(g),$$
 is



9. At constant pressure, the heat of combustion of carbon monoxide at

 $17^{0}C$  is -284.5 kl. Calculate its heat of combustion at constant volume



**10.** What is the work done in a open vessel at  $27^{\circ}C$ , when 92 grams of sodium metal reacts with water.



11. Certain amount of argon at 1 atm and 300 K expands reversibly and adiabatically from 1.25 Lto 2.5 L. If  $C_v$  for Ar is  $12.48JK^{-1}mol^{-1}$ , calculate the enthalpy charge.



12. In an insulated container, 1 mole of a liquid of molar volume 100 mL is at 1 bar. If the liquid is steeply taken to 100 bar, the volume of liquid decreases by 1 mL. Find the work done and  $\Delta H.$ 



**13.** HCI is a strong acid, but HF is a weak acid. The enthalpy of neutralisation of HCl is -57.3 kJ  $mol^{-1}$  and of HF is -68.3 kl.  $mol^{-1}$ . Explain.



**14.** The enthalpy of vapourisation of water is 37.3 kl  $mol^{-1}$ . Calculate the molar entropy of vapourisation of water.



**15.** The standard enthalpy of hydrogenation of cyclohexene is119 kJ $mol^{-1}$  . If enthalpies for formation of cyclohexane and benzene at  $25^{\circ}C$  are

respectively -156 and + 49 kJ  $mol^{-1}$  , estimate the magnitude of resonance energy of benzene.



**16.** Calculate the number of calories of energy released when 1 L of HCI is formed at 1 atm and  $25\,^{\circ}\,C$ . The dissociation energies of gaseous  $H_2,\,Cl_2$  and HCl are respectively 104, 58 and 103 K cal  $mol^{-1}$ .



17. Heats of atomisation of  $NH_3$  and  $NH_2H_4$  are  $xKJmol^{-1}$  and  $yKJmol^{-1}$ respectively. What is the average energy of N-N bond ?



**18.** Standard enthalpies of  $C_6H_6(l), H_2O(g)$  and  $CO_2(g)$  are respectively 11.7, -68.3 and -94 kCal. Calculate the calorific value of benzene.



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**19.** Heat of formation of water and heats of combustion of ethylene and acetylene are respectively  $286,\ -1410\ {
m and}\ -1299kJmol^{-1},$  Calculate the heat of the reaction,

$$C_2 H_{2\,(\,g\,)} \, + H_{2\,(\,g\,)} \, o C_2 H_{4\,(\,g\,)} \, .$$



**20.** At  $427^{\circ}C$ , for a given change the values of  $\Delta G$  and  $\Delta H$  are  $-11,500Jmol^{-1}$  and  $-11,300Jmol^{-1}$  respectively. Calculate the value of  $\Delta S$ .



**21.** Calculate the entropy change when one kg of water is heated from  $27^{\circ}C$  to  $200^{\circ}C$  forming super heated steam under constant pressure. Specific heat of water and systems are respectively 4180 and  $1670+0.49\frac{J}{ka}-K$ .



**22.** Standard entropies of $H_2(g), O_2(g)$  and  $H_2O(l)$  are respectively 126.6, 201.2 and  $68JK^{-1}mol^{-1}$  Determine  $\Delta S$  for  $2H_2(g)+O_2(g)\to 2H_2O(l)$  at  $25^\circ C$ .



**23.** At  $127^{\circ}C, K_c$  for  $2A \Leftrightarrow 2B+C$  is  $2\times 10^{-4}.$  Calculate  $\Delta G^{\circ}$  for the reaction.



**24.** The standard heats of formation values of  $SF_6(g)$ , S(g) and F(g) are respectively -100, 275 and 80 kJ  $mol^{-1}$ . Estimate the average S-F bond energy sulphur herafluoride.



**25.** lodine molecule dissociates into atoms after absorbing light of 4500 Å. If one quantum of radiation is absorbed by each molecule, calculate the kinetic energy of iodine atoms. Bond energy of  $I_2$  is  $240kJmol^{-1}$ 



**26.** Suggest the conditions for the spontaneity the thermal decomposition of lime stone.



**27.** The reaction  $A+B\Leftrightarrow C$  has the value of  $\Delta H$  and value of  $\Delta S$ respectively -12.52kJ and  $313 Jmol^{-1}K^{-1}$ .At What temperature the reaction attains equilibrium state.



28.

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$$HC_2H_2ClO_2(aq) \Leftrightarrow H^+ + C_2H_2ClO_2^-(aq)HCH, C/O(aq) = H + CHC$$

For

the equillibrium constant at  $25^{\circ}C$  is  $1.35 imes 10^{-3}M$ . Calculate  $\Delta G^{\circ}$  .

the

reaction,

**View Text Solution** 

