CHEMISTRY

FOR IIT JEE ASPIRANTS OF CLASS 12 FOR CHEMISTRY

THERMOCHEMISTRY

Illustration

1. The $\Delta_f H^\circ(N_2O_5, g)$ in kJ/mol on the basic of the following data is:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta_r H^\circ = -114 \text{ kJ/mol}$

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g) \quad \Delta_r H^\circ = -102.6 \text{ kJ/mol}$

$\Delta_f H^\circ(NO, g) = 90.2 \text{ kJ/mol}$

A. 15.1

B. 30.2

C. -36.2

D. None of these

Answer: A

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2. The heat of combustion of sucrose, $C_{12}H_{22}O_{11}(s)$ at constant volume is - 1348.9 kcal mol^{-1} at $25^{\circ}C$ then the heat of reaction at constant pressure, when stem is produced, is

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3. The heats of combustion of yellow phosphorus and red phosphorous are - $9.19KJ$ and - $8.78KJ$ respectively, then heat of transition of yellow phosphorus to red phosphorous is

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4. For the reaction

$N_2H_4(g) \rightarrow N_2H_2(g) + H_2(g) \quad \Delta_r H^{\circ} = 109KJ/mol$

Calculate the bond enthalpy of $N = N$.

Given :

$B.\ E.\ (N - N) = 163KJ/mol,\ B.\ E.\ (N - H) = 391KJ/mol,\ B.\ E.\ (H$

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5. Calculate lattice energy for the change,

$Li^+(g) + Cl^-(g) \rightarrow LiCl(g)$

Given that

$\Delta H_{\text{sublimation}}$ of $Li = 160.67kJmol^{-1}$, $\Delta H_{\text{Dissociation}}$ of $Cl_2 = 244.$

$\Delta H_{\text{ionisation}}$ of $Li(g) = 520.07kJmol^{-1}$, $\Delta H_{E.A}$ of $Cl(g) = -365.$

ΔH_f of $LiCl(s) = -401.66kJmol^{-1}$,

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6. 100 gm of anhydrous $CuSO_4$, when dissolved in excess of water produces 42 kJ of heat. The same amount of $CuSO_4.5H_2O$ on dissolving in large excess of water absorbed 4.60 kJ. What is the heat of hydration $CuSO_4$?

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7. Heat of neutralization (ΔH) of NH_4OH and HF are -51.5 and $-68.6kJ$ respectively. Calculate their heat of dissociation?

(i) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O, \quad \Delta H = -57.3kJ$

(ii)

$$\underset{\text{(weak base)}}{HCl(aq) + NH_4OH(aq)} \rightarrow NH_4Cl(aq) + H_2O, \quad \Delta H = -51.5kJ$$

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8. Calculate resonance energy of $C_6H_6(g)$.

Given : $\Delta_f[C_6H_6(g)] = -360kJmol^{-1}$

$\Delta H_{\text{Sub}}[C(\text{graphite})] = 716kJmol^{-1}$

$B.E._{H-H} = 437kJmol^{-1}$

$B.E._{C=C} = 620kJmol^{-1}$

$B.E._{C-C} = 340kJmol^{-1}$

$B.E._{C-H} = 490kJmol^{-1}$

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9. A calorimeter will heat capacity equivalent to having 13.3 moles of water is used to measured the heat of combustion from $0.303g$ of sugar $(C_{12}H_{22}O_{11})$. The temperature increase was found to be $5.0K$. Calculate the heat released, the amount of heat released by $1.0g$, and 1.0 mole of sugar.

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10. The temperature of a calorimeter increases $0.10K$ when $7.52J$ of electric energy is used to heat it. What is the heat capacity of the calorimeter?

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11. When $0.1025g$ of benzoic acid was burnt in a bomb calorimeter the temperature of the calorimeter increased by $2.165^{\circ}C$. For benzoic acid $\Delta H^{\circ}_{\text{comb}} = -3227kJmol^{-1}$. Calculate the heat capacity of the calorimeter.

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Solved Example

1. Benzene burns according to the following equation

$$2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l) \quad \Delta H^\circ = -6542KJ$$

What is the ΔE° for the combustion of 1.5 mol of benzene

A. $-3271KJ$

B. $-9813kJ$

C. $-4906.5kJ$

D. None of these

Answer: D

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2. What is the value of change in internal energy at 1 at, in the process

$H_2O(l, 323K) \rightarrow H_2O(g, 473K)$

Given :

$C_p(H_2O, l) = 75.3JK^{-1}mol^{-1}, C_p(H_2O, g) = 33.314JK^{-1}mol^{-1}, \Delta H_{vap}$

at $373K = 40.7kJ/mol$

A. $109.1kJ/mol$

B. $37.6KJ/mol$

C. $43.86KJ/mol$

D. $48.36KJ/mol$

Answer: C

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3. Given : $S_{(s)} + \frac{3}{2}O_{2(g)} \rightarrow SO_{3(g)} + 2XKcal$

$SO_{2(s)} + \frac{1}{2}O_{2(g)} \rightarrow SO_{3(g)} + YKcal$

The heat of formation of SO_2 is : $-$

A. $(y - 2x)$

B. $(2x + y)$

C. $(x + y)$

D. $2x / y$

Answer: A

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4. The molar heat capacities at constant pressure (assumed constant with respect to temperature) of A, B and C are in ratio of $1.5 : 3.0 : 2.5$. If enthalpy change for the exothermic reaction $A + 2B \rightarrow 3C$ at $300K$ and $310K$ is ΔH_1 and ΔH_2 respectively then

A. $\Delta H_1 > \Delta H_2$

B. $\Delta H_1 < \Delta H_2$

C. $\Delta H_1 = \Delta H_2$

D. If $T_2 > T_1$ then $\Delta H_2 > \Delta H_1$ 7 if $T_2 < T_1$ then $\Delta H_2 < \Delta H_1$

Answer: C

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5. Solid $CaSO_4.2H_2O$ is taken in a container fitted with a frictionless piston initially containing no other gases. The external pressure is maintained at 1 atm and the container is heated till the equilibrium is achieved.

$CaSO_4.2H_2O(s) \Rightarrow 2CaSO_4(s) + 2H_2O(g)$

If $\Delta H^\circ = +30Kcal/mol$ and $\Delta S^\circ = +40cal/K$, at what temperature equilibrium will be establised in the container. (Ignore variation of ΔH_0 and ΔS_0 with temperature)

A. 600 K

B. 750 K

C. 700 K

D. 300 K

Answer: B

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6. For the reaction

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

using data given in table find out incorrect statement (s) among the following

	$\Delta H_f^\circ (kJ/\text{mole})$	$S^\circ (J/K\text{mole})$
$CO(g)$	-110	$+197$
$O_2(g)$	0	$+205$
$CO_2(g)$	-395	$+213$

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

A. $\Delta H^\circ > \Delta U^\circ$ for the reaction at 298 K

B. In standard state conditin, the rection $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ attain equilibrium at very hight temperature.

C. At low temperature $\frac{d(\Delta H)^{\circ}}{dT} = -ve$

D. In a CO, O_2 fuel cell electrical energy obtained by cell $> \left|\Delta H^{\circ}_{\text{combustion}}[CO(g)]\right|$

Answer: A

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7. The heat of vaporisation : ΔH_{vap}, of CCl_4 at $27^{\circ}C$ is 42 kJ/mole

$CCl_4(l) \rightarrow CCl_4(g) : \Delta H_{\text{vap}} = 42.0 kJ/\text{mole}$

If 1 mole of liquid $\mathbb{C}l_4$ at $27^{\circ}C$ has entropy of 214 J/K mole, what is the entropy (in J/K-mol) of 1 mole of vapour in equilibrium with liquid at this temperature.

A. 74

B. 454

C. 354

D. 254

Answer: C

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8. If $\Delta H_{\text{vaporisation}}$ of substance $X(l)$ (molar mass : $30g/mol$) is 300 J/g at it's boling point 300 K , then molar entropy change for reversible condensation process is

A. $30J/mol.\ K$

B. $-300J/mol.\ K$

C. $-30J/mol.\ K$

D. none of these

Answer: C

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9. The following sequence of reaction occurs in commercial production of aqueous of aqueous nitric acid.

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l) \quad \Delta H = -904kJ \ldots . (1)$$
$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \quad \Delta H = -112kJ \ldots . (2)$$
$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g) \quad \Delta H = -140kJ \ldots . (3)$$

Determine the total heat liberated (in kJ/mol) at constant pressure for the production of exactly 1 mole of aqueous nitric acid from NH_3 by this process.

A. 986

B. 493

C. 246.5

D. none of these

Answer: B

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10. If $\Delta H_{\text{vaporisation}}$ of $(C_2H_5)O(l)$ is $350J/g$ at it's boiling point 300 K, then molar entropy change for condensation process is

A. $86.33J/mol.K$

B. $-86.33J/mol.K$

C. $-1.16J/mol.K$

D. 1.16

Answer: B

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11. Calculate ΔG (in kJ) for the reaction at 300 K,

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

Given at 300 K,

$BE_{H-H} = 435kJmol^{-1}, BE_{Cl-Cl} = 240kJmol^{-1}, BE_{HCl} = 430kJmol^{-1}$

Entropies of H_2, Cl_2 and HCl are 131, 223 and $187JK^{-1}mol^{-1}$ respectively.

A. 191

B. 291

C. -191

D. None of these

Answer: C

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12. $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g), \quad \Delta H_1$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g), \quad \Delta H_2$

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g), \quad \Delta H_3$

The heat of formation of NCl_3 in the terms of ΔH_1, $\Delta H_2 \text{and} \Delta H_3$ is

A. $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

B. $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

C. $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

D. None

Answer: A

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13. If $Ag_2O(s)$ is ecposed to atmosphere having pressure 1 atm and temperature 1 atm and temperature $27^\circ C$. Under these conditions comment whether it will dissociate spontaneously or not.

$2Ag_2O(s) \Leftrightarrow 3Ag(s) + O_2(g)$

Given :	ΔH_f° (kJ/mol)	ΔS° (J/K mol) at $27^\circ C$
$Ag(s)$	0	42.0
$Ag_2O(s)$	-30	121.0
$O_2(g)$	0	204.0

(Air consist of 20 % O_2 by volume)

Take : $R = 8.3JK^{-1}mol^{-1}$

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14. A 500 gm sample of water is reacted with an equimolar amount of CaO (both at an initial temp of $25^\circ C$). What is the final temperature of the product? [Assume that the product absorbs all of the heat released in

the reaction] Heat produced per mol of $Ca(OH)_2$ is $65.2kJ$ and specific heat $Ca(OH)_2$ is $1.2J/g^\circ C$.

A. $\approx 735^\circ C$

B. $\approx 760^\circ C$

C. $\approx 746^\circ C$

D. $\approx 789^\circ C$

Answer: B

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15. The enthalpy of formation of enthane and benzene from the gaseous atoms are -2839.2 and $-5506kJ/mol$ respectively. Bond enthalpy of $C=C$ bond is

Given: Resonance energy of benzene $= -23.68$ kJ/mol

Bond enthalpy of $C-H$ bond $= 411.0$ kJ/mol

A. 373.98 kJ/mol

B. 632.24 kJ/mol

C. 647.5 kJ/mol

D. 1896.72 kJ/mol

Answer: B

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16. The reaction $CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$ has $\Delta H = -25$ kCal.

Bond	Bond Energy k Cal
ε_{C-Cl}	84
ε_{H-Cl}	103
ε_{C-H}	x
ε_{Cl-Cl}	y

$x : y = 9 : 5$

From the given data, what is the bond energy of $Cl - Cl$ bond (in k.cal)

A. 70 kCal

B. 80 kCal

C. 67.75 kCal

D. 57.75 kCal

Answer: D

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17. Ethyl chloride (C_2H_5Cl) , is prepared by reaction of ethylene with hydrogen chloride:

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g) \qquad \Delta H = -72.3KJ/\text{mol}$

What is the value of $\Delta E(\text{in KJ})$, if 98 g fo ethylene and 109.5 g if HCl are allowed to react at 300K

A. -64.81

B. -190.71

C. -209.41

D. -224.38

Answer: C

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18. (i) Determine $\Delta_f H^\circ(NO, g)$ at $25^\circ C$. Using the following information

$\Delta_f H^\circ(CO_2, g) = -393.5$ kJ/mol

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)(g) \qquad \Delta_r H^\circ = -114.0 \text{ kJ/mol}$

$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta_r H^\circ = -566.0 \text{ kJ/mol}$

$4CO(g) + 2NO_2(g) \rightarrow 4CO_2(g) + N_2(g) \qquad \Delta_r H^\circ = -1198.4 \text{ kJ/mo}$

(ii) Calculate the equilibrium pressure (in Pascal) for the conversion of grapgite to diamond at $25^\circ C$. The densities of graphite and diamond may be taken to be 2.20 and 3.40 g/cc respectively independent of pressure.

Given : $\Delta G^\circ(C(\text{graphite}) \rightarrow C(\text{diamond})) = 2900$ J/mol.

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19. Which of the following do(es) not represent ΔH formation of the product.

$(I)\frac{1}{2}H_2(g) + (aq) \rightarrow H^+(aq) \qquad (II)\frac{2}{3}O_3(g) \rightarrow O_2(g)$

$(III) NH_4^+(g) + Cl^-(g) \rightarrow NH_4Cl(s)$ $(IV) P_4(\text{black}) + 5O_2(g) \rightarrow P_4$

(V) Reaction representing $\Delta H_{\text{combustion}}$ of C (graphite).

A. I, IV, V

B. II, IV

C. II, III, IV

D. II, III, IV, V

Answer: C

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20. White phosporus is a tetra-atomic solid $P_4(s)$ at room temperature.

Find average $(P - P)$ bond enthalpy in kJ/mol.

$$\text{Given}: \quad \Delta H_{\text{sublimation}} \text{ of } P_4(s) = 59 \text{ kJ/mol}$$
$$\Delta H_{\text{atomisation}} \text{ of } P_4(s) = 1265 \text{ kJ/mol}$$

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21. Calculate the strength of H-bond between $F^-(g)$ and $CH_3COOH(g)$

from the given data.

$$\begin{aligned}
&\Delta H_{\text{solution}}[KF.CH_3COOH(s)] \text{ in glacial acetic acid} &&= -3 \text{ kJ/mole} \\
&\Delta H_{\text{solution}}[KF(s)] \text{ in glacial acetic acid} &&= +35 \text{ kJ/mole} \\
&\text{Lattice Enthalpy KF(s)} &&= +797 \text{ kJ/mole} \\
&\text{Lattice enthalpy of } KF.CH_3COOH(s) &&= +734 \text{ kJ/mole} \\
&\Delta H_{\text{vaporization}}[CH_3COOH(l)] &&= +21 \text{ kJ/mole}
\end{aligned}$$

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22. Find the bond enthalpy (in kJ/mol) of one "three centre two electron bond" in $B_2H_6\{B-H-B \rightarrow 2B(g)+H(g)\}$ from the given data.

$\Delta H_f^\circ[BH_3(g)] = 100 \text{ kJ/mole}$ $\Delta H_f^\circ[B_2H_6(g)] = 36 \text{ kJ/mole}$

$\Delta H_{\text{atm}}[B(s)] = 565 \text{ kJ/mole}$ $\Delta H_{\text{atm}} = [H_2(g)] = 218 \text{ kJ/mole}$

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23. For the reaction

$$CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

using data given in table find out incorrect statement(s) among the following.

	$\Delta H_f^\circ\,(\mathrm{kJ/mole})$	$S^\circ\,(\mathrm{J/Kmole})$
$CO(g)$	-110	$+197$
$O_2(g)$	0	$+205$
$CO_2(g)$	-395	$+213$

Assume vibration modes of motion do not contribute to heat capacity at low temperature.

A. $\Delta H^\circ > \Delta U^\circ$ for the reaction at 298 K.

B. In standard state condition, the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ attain equilibrium at very high temperature.

C. At low temperature $\frac{D(\Delta H)^\circ}{dT} = -ve$

D. In a CO, O_2 fuel cell electrical energy obtained by cell $> \left|\Delta H^\circ_{\text{combustion}}[CO(g)]\right|$

Answer: A

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24. At temperature above 85 K, decarboxylation of acetic becomes a spontaneous process under standard state conditions. What is the standard entropy change (in J/K-mol) of the reaction.

$$CH_3COOH(aq) \rightarrow CH_4(g) + CO_2(g)$$

$$\begin{aligned} \text{Given}: \quad \Delta H_f^\circ [CH_3COOH(aq)] &= -484 \text{ kJ/mole} \\ \Delta H_f^\circ [CO_2(g)] &= -392 \text{ kJ/mole} \\ \Delta H_f^\circ [CH_4(g)] &= -75 \text{ kJ/mole} \end{aligned}$$

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25. The enthalpy changes of the following reactions at $27^\circ C$ are

$$\begin{aligned} Na(s) + \tfrac{1}{2}Cl_2(g) &\rightarrow NaCl(s) & \Delta_r H &= -411 \text{ kJ/mol} \\ H_2(g) + S(s) + 2O_2(g) &\rightarrow H_2SO_4(l) & \Delta_r H &= -811 \text{ kJ/mol} \\ 2Na(s) + S(s) + 2O_2(g) &\rightarrow Na_2SO_4(s) & \Delta_r H &= -1382 \text{ kJ/mol} \\ \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g) &\rightarrow HCl(g) & \Delta_r H &= -92 \text{ kJ/mol}, \quad R = \end{aligned}$$

from these data, the heat change of reaction at constant volume (in kJ/mol) at $27^\circ C$ for the process $2NaCl(s) + H_2SO_4(l) \rightarrow Na_2SO_4(s) + 2HCl(g)$ is

A. 67

B. 62.02

C. 71.98

D. None

Answer: B

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26. Calculate $\left|\Delta_f G^\circ\right|$ for $(NH_4Cl,\, s)$ at $350K$.

Given : $\Delta_f H^\circ(NH_4Cl,\, s) = -314.5\ \text{kJ/mol}$

$\left(S^\circ_{N_2(g)} = 192JK^{-1}mol^{-1},, S^\circ_{H_2(g)} = 130.5JK^{-1}mol^{-1},\right), \left(S^\circ_{Cl_2(g)} =\right.$

$\left(\Delta_r C_P = -20\ \text{J/mol-K},, \ln\left(\frac{350}{300}\right) = 0.15,\right)$

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27. If enthalpy of hydrogenation of $C_6H_6(l)$ into $C_6H_{12}(l)$ is $-205kJ$ & resonance energy of $C_6H_6(l)$ -152 kJ/mol then enthalpy of hydrogenation

of 1, 4-cyclohexadiene (l) is

Assume ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ all are equal

A. -535.5 kJ/mol

B. -238 kJ/mol

C. -357 kJ/mol

D. None

Answer: B

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28. The enthalpy of gas phase trimerization of one mole of gaseous formaldehyde in (kJ/mole)

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29. Calculate the enthalpy change for the given reaction from data provided (kJ/mole)

$$\underset{\text{(weak acid)}}{HA(g)} + \underset{\text{(weak acid)}}{B(g)} \longrightarrow \underset{\text{(Salt)}}{AHB(s)}$$

$\Delta H_{\text{neutralization}}\{HA(aq)[\text{at infinite dilution}]\,/\,B(aq)[\text{at infinite dilution}]\} =$

$$\Delta H_{\text{solution}}[HA(g)] = -10 \text{ kJ/mole} \quad \{\text{at infinite dilution}\}$$
$$\Delta H_{\text{solution}}[B(g)] = -5 \text{ kJ/mole} \quad \{\text{at infinite dilution}\}$$
$$\Delta H_{\text{solution}}[HAB(s)] = +8 \text{ kJ/mole} \quad \{\text{at infinite dilution}\}$$

A. -36

B. -63

C. -45

D. -37

Answer: B

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30. Estimate $\Delta H_f^\circ\{\text{pyridine} \quad (l)\}$ from the given data.

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31. The standard enthalpy of atomisation of $PCl_3(g)$ is $195\ \mathrm{Kcal/mol}$. What will be the standard enthalpy of atomisation of $PCl_5(g)$, if the bond dissociation energies of axial $P-Cl$ bonds in $PCl_5(g)$ are $10\,\%$ lesser and the bond dissociation energies of equatorial $P-Cl$ bonds in $PCl_5(g)$ are $10\,\%$ higher than the bond dissociation energies of $P-Cl$ vonds in $PCl_3(g)$.

A. 195 K cal/mol

B. 325 K cal/mol

C. 331.5 K cal/mol

D. 318.5 K cal/mol

Answer: C

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32. An important reaction in production of smog is

$NO_2(g) + hv \rightarrow NO(g) + O(g)$

If light of wavelength $4.4 \times 10^{-7} m$ is used to cause above reaction. Calculate $N - N$ bond enthalpy.

Given : $\Delta H_f[NO(g)] = 91 \text{ kJ mol}^{-1}$ $h = 6.6 \times 10^{-34} Js$

$\Delta H_f[N_2O_4(g)] = 9 \text{ kJ mol}^{-1}$ $c = 3 \times 10^8 ms^{-1}$

$\Delta H_{O=O} = 498 \text{ kJ mol}^{-1}$ $N_A = 6 \times 10^{23}$

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Exercise

1. How much heat will be required at constant pressurent to form $1.28kg$ of CaC_2 from $CaO(s)$ & $C(s)$?

Given : $\Delta_f H^\circ(CaO,s) = -152kcal/mol$

$\Delta_f H^\circ(CaC_2,s) = -14kcal/mol$

$\Delta_f H^\circ(CO,g) = -26kcal/mol$

A. $+112$ kcal

B. 224 kcal

C. 3840 kcal

D. 2240 kcal

Answer: D

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2. (1) For the given heat of reaction,

(i) $C(s) + O_2(g) = CO_2(g) + 97kcal$

(ii) $CO_2(g) + C(s) = 2CO(g) - 39kcal$

the heat of combustion of $CO(g)$ is:

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3. Calculate the heat of transition for carbon from the following:

$C_{\text{Diamond}} + O_2 \rightarrow CO_2(g), \Delta H = -94.3kcal$

$C_{\text{Amorphous}} + O_2 \rightarrow CO_2(g), \Delta H = -97.6kcal$

Also calculate the heat required to change $1g$ of C_{Diamond} to $C_{\text{Amorphous}}$.

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4. What is the Bond energy (In kJ/ mol) of $C-H$ in Methane from the following data?

$$\begin{aligned}
\Delta H_f[CO_2(g)] &= -394\text{kJ/mol} \\
\Delta H_f[H_2O(l)] &= -285\text{kJ/mol} \\
\Delta H_{\text{siblimation}}\{\text{Carbon (graphite)}\} &= +716\text{kJ/mol} \\
\Delta H_{\text{combustion}}[CH_4(g)] &= -890\text{kJ/mol} \\
\text{Bond energy}(H-H) &= 435\text{kJ/mol}
\end{aligned}$$

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5. Calculate $\Delta_{\text{neut}}H$ of HA. If bond dissociation energy of $H-A$ is $5KJ/\text{mol}$

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6. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at $25^\circ C$ are -156 and $+49KJmol^{-1}$ respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at $25^\circ C$ is

$-119 l mmol^{-1}$. Use these data to estimate the magnitude of the resonance energy of benzene.

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7. The heat released by one mole of sugar from a bomb calorimeter ecperiment is $5648 KJ/mol$. Calculate the enthalpy of combution per mole of sugar.

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8. When $0.7022 g$ of oxalic acid $(C_2O_4H_2)$ is burnt in the calorimeter. The temperature. The temperature increased by $1.602^\circ C$. The heat capacity of the calorimeter is $1.238 KJ/K$. Calculate ΔH° comb.

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Exercise 1

1. For which change $\Delta H \neq \Delta E$:-

A. $H_2(g) + I_2(g) \rightarrow 2HI(g)$

B. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

C. $C(s) + O_2(g) \rightarrow CO_2(g)$

D. $N_g + 3H_2(g) \rightarrow 2NH_3(g)$

Answer: D

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2. Reactions involving gold have been of particular interest to a chemist.

Consider the following reactions,

$$Au(OH)_3 + 4HCl \rightarrow HAuCl_4 + 3H_2O, \quad \Delta H = -28kCal$$
$$Au(OH)_3 + HBr \rightarrow HAuBr_4 + 3H_2O, \quad \Delta H = -36.8kCal$$

In an experiment there was an absorption of 0.44 k Cal when one mole of $HAuBr_4$ was mixed with 4 moles of HCl. what is the percentage conversion of $HAuBr_4$ into $HAuCl_4$?

A. 0.005

B. 0.006

C. 0.05

D. 0.5

Answer: C

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3. If x_1, x_2 and x_3 are enthalpies of H-H , O=O and O-H bonds respectively , and x_4 is the enthalpy of vaporisation of water , estimate the standard enthalpy of combustion of hydrogen:

A. $x_1 + \frac{x_2}{2} - 2x_3 + x_4$

B. $X_1 + \frac{x_2}{2} - 2x_3 - x_4$

C. $x_1 + \frac{x_2}{2} - x_3 + x_4$

D. $2x_3 - x_1 - \frac{x_2}{2} - x_4$

Answer: B

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4. For the allotropic change represented by the equation C (graphit) $\rightarrow$ C (diamond), $\Delta H = 1.9kJ$. If 6g of diamond and 6 g of graphite are separately burnt to yield CO_2, the enthalpy liberated in first case is

A. less than in the second case by 1.9 kJ

B. more than in the seocnd in first case is

C. more than in the second case by 0.95 kJ

D. less than in the second case by 11.4 kJ

Answer: C

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5. Given :

(i) $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g), \Delta H_1$

(ii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)\ , \Delta H_2$

(iii) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)\ , \Delta H_3$

Express the enthalpy of formation of $NCl_3(g)\left(\Delta H_f\right)$ in terms of ΔH_1, ΔH_2 and ΔH_3:

A. $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

B. $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

C. $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

D. None

Answer: A

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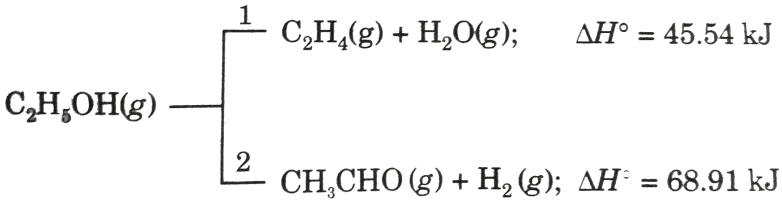
6. Ethanol can undergo decompostion to form two sets of products.

If the molar ratio of $C_4H_4 \text{to} CH_3CHO$ is 8:1 in a set of product gases,

then the energy involved in the decomposition of 1 mole of ethanol is:



A. 65.98 kJ

B. 48.137 kJ

C. 48.46 kJ

D. 48.46 kJ

Answer: B

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7. Find $\Delta_r U^\circ$ for the reaction $4HCl(g) + O_2(g) \Rightarrow 2Cl_2(g) + 2H_2O(g)$

at 300 K. Assume all gases are ideal

Given $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta_r H^\circ_{300} - 184.5kJ/\text{mole}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\Delta_r H^\circ_{300} = -483kJ/\text{mole}(\text{Use}R =$

A. 111.5 kJ/mole

B. $-109.01kJ/\text{mole}$

C. $-111.5kJ/\text{mole}$

D. None

Answer: C

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8. The enthalpy change of the following reactions at $27^\circ C$ are

$\left(Na(s)+\frac{1}{2}Cl_2 \rightarrow NaCl(s), \Delta_r H = -411kJ/\text{mol}, \right), (H_2(g)+S(s)+$

$(2Na(s)+S(s)+2O_2(g) \rightarrow Na_2SO_4(s), \Delta_r H = -1382kJ/\text{mol},), \left(\frac{1}{2}$

form these data, the heat change of reaction at constant volume (in KJ/mol) at $27^\circ C$ for the process $2NaCl(s)+H_2SO_4(l) \rightarrow Na_2SO_4(s)+2HCl(g)$ is

A. 67

B. 62.02

C. 71.98

D. None

Answer: B

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9. What is the ratop of the enthalpy yield on combustion of hydrogen of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam ?

Given: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g), \Delta H = -242kJ$

$B.E.(H - H) = 436kJ$

A. $0.80:1$

B. $1:0.80$

C. $1.80:1$

D. $1.80:1$

Answer: D

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10. The molar heat capacities at constant pressure (assume constant with respect to temperature) of A, B and C are in ratio of $1.5:3.0:2.0$. If enthalpy change for the exotherimic reaction $A+2B\rightarrow 3C$ at $300K$ is $-10kJ/\text{mol}$ & $C_{p.m}$ (B) is 300 J/mol then enthalpy change at 310 K is:

A. $-8.5kJ/mol$

B. $8.5kJ/mol$

C. $-11.5kJ/mol$

D. none of these

Answer: C

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11. The lattice enthalpy of solid $NaCl$ is $772kJmol^{-1}$ and enthalpy of solution is $2kJmol^{-1}$. If the hydration enthaply of Na^+ & Cl^- ions are in the ratio of $3:2.5$, what is the enthalpy of hydration of chloride ion ?

A. $-140kJmol^{-1}$

B. $-350kJmol^{-1}$

C. $-351.81mol^{-1}$

D. None

Answer: B

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12. ΔH_f° of water is -285.5 KJ mol^{-1}. If enthalpy of neutralisation of monoacid strong base is -57.3 KJ mol^{-1}, ΔH_f° of OH^- ion will be

A. $-228.5kJmol^{-1}$

B. $228.5kJmol^{-1}$

C. $114.25 kJmol^{-}$

D. $-114.25 kJmol^{-1}$

Answer: A

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13. Select the correct option.

A. $\Delta H_f[H(g)]$ is equal to $\Delta H_{\text{atomisaation}}$ of $H_2(g)$

B. $\Delta H_{BE}(H-H)$ is equal to ΔH_f of

C. $\Delta H_{BE}(H-H)$ is equal to $\Delta H_{\text{atomisation}}$ of $H_2(g)$

D. $\Delta H_{\text{comustion}}[H_2(g)]$ is equal to $\Delta H_f[H_2(g)]$

Answer: C

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14. The standard enthalpy of formation of ammonia gas is

Given: $N_2H_4(g) + H_2(g) \rightarrow 2NH_3(g), \Delta H_r^\circ = -40kJ/mol$

$\Delta H_f^\circ [N_2H_4(g)] = -120kJ/mol$

A. -60

B. -180

C. 40

D. -80

Answer: D

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15. Study the following therochemical equations:

$$A \longrightarrow B \qquad \Delta H = +100Kcal$$
$$B \longrightarrow C \qquad \Delta H = -80Kcal$$

The correct order of enthapies of formation of A, B and C is

A. $A < B < C$

B. $A < C < B$

C. $C < A < B$

D. $B < C < A$

Answer: B

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16. Select the option in which heat evolved is maximum.

Given :

$\Delta_f H^\circ(CO_2, g) = -75kCal/mol, \quad \Delta_f H^\circ(CO, g) = -25kCal/mol$

The product will be CO if excess amount of carbon is present and CO_2 if excess O_2 is present

A. 10 moles of carbon and 4.5 moles of O_2

B. 24 gm of carbon and 64 gm of O_2

C. 4 moles of carbon and 3.5 moles of O_2

D. 30 gm of carbon and 80 gm of O_2

Answer: C

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Exercise 2

1. An stoichiometric mixture of hydrogen gas and the air at $25^{\circ}C$ and a total pressure of 1 atm, is exploded in a closed rigid vessel. If the process occurs under adiabatic condition then using the given data answer the question that follow:

Given : (i)

$C_P = 8.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, (ii) C_P = 11.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, \Delta H_f[H_2$

[Take air as $80\ \%\ N_2$, $20\ \%\ O_2$ by volume]

The value of C_P of N_2 & H_2O will be (in Cal.deg.$^{-1}$ mol^{-1})

A. 8.3, 8.3

B. 8.3, 11.3

C. 113, 11.3

D. 11.3, 8.3

Answer: B

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2. An stoichiometric mixture of hydrogen gas and the air at $25^{\circ}C$ and a total pressure of 1 atm, is exploded in a closed rigid vessel. If the process occurs under adiabatic condition then using the given data answer the question that follow:

Given : (i)

$C_P = 8.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, (ii) C_P = 11.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, \Delta H_f[H_2$

[Take air as $80\ \%\ N_2$, $20\ \%\ O_2$ by volume]

What will be the maximum temperature attained if the process occurs in adiabatic container ?

A. $\cong 2937K$

B. $\cong 2665K$

C. $\cong 1900K$

D. $\cong 298K$

Answer: A

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3. An stoichiometric mixture of hydrogen gas and the air at $25^{\circ}C$ and a total pressure of 1 atm, is exploded in a closed rigid vessel. If the process occurs under adiabatic condition then using the given data answer the question that follow:

Given : (i)

$C_P = 8.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, (ii) C_P = 11.3 \ \text{Cal deg}^{-1} \ \text{mol}^{-1}, \Delta H_f[H_2$

[Take air as $80\ \%\ N_2$, $20\ \%\ O_2$ by volume]

What will be final pressure in atm ?

A. $\cong 8.5$

B. $\cong 7.6$

C. $\cong 5.46$

D. $\cong 0.85$

Answer: A

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4. A mixture of hydrogen gas and theortical amount of air at 25° C and a total pressure of 1atm , is exploded in a closed right vessel . If the process ossurs under adiabatic conditions then using the given data anwer the question that follow :

Given :

$C_p(N_2)$ and $C_p(H_2O)$are8.3 and $11.3 cal deg^{-1} mol^{-1}$ not necessarily in the same order.

$\Delta H_f[H_2O(g)] = -57.8 kcal$

[take air as $80\ \% N_2, 20\ \% O_2$by volume.]

If at a initial temperature $T_1, (e_1)$ is initial energy and higher final temperature ,T_2, E_2 is the final internal energy , then which option is true?

A. $E_1 > E_2$

B. $E_2 > E_1$

C. $E_1 = E_2$

D. can't be compared from the given data

Answer: C

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5. Statement-I : The enthalpy of neutralization of the reaction between HCl and $NaOH$ is -13.7 kCal/mol. If the enthalpy of neutralization of oxalic acid $(H_2C_2O_4)$ by a strong base is -25.4 kCal/mol, then the enthalpy change $(|\Delta_r H|)$ of the process $H_2C_2O_4 \rightarrow 2H^+ + C_2O_4^{2-}$ is 11.7 kCal/mol.

Statement-II : $H_2C_2O_4$ is a weak acid.

A. If both Statement-I & Statement-II are True & the Statement-II is a correct explanation of the Statement-I

B. If both Statement-I & Statement-II are True but Statement-II is not a correct explanation of the Statement-I

C. If statement-I is True but the Statement-II is False.

D. If Statement-I is False but the Satement-II is True

Answer: D

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6. Statement-I : Standard enthalpy of isomerisation of an anatiomer into the other is zero.

Statement-II : The two enantiomers of any chiral compound have the same enthalpy of formation.

A. If both Statement-I & Statement-II are True & the Statement-II is a correct explanation of the Statement-I

B. If both Statement-I & Statement-II are True but Statement-II is not a correct explanation of the Statement-I

C. If statement-I is True but the Statement-II is False.

D. If Statement-I is False but the Satement-II is True

Answer: A

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7. $100ml0.25MH_2SO_4$ (strong acid) is neutralised with 200 ml $0.2MNH_4OH$ in a constant pressure Calorimeter which results in temperature rise of $1.4^\circ C$. If heat capacity of Calorimeter constent is $1.5kJ/^\circ C$. Which statement is/are correct

Given : $HCl + NaOH \rightarrow NaCl + H_2O + 57kJ$

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O + 48.1kJ$

A. Enthalpy of neutralisation of HCl v/s NH_4OH is -52.5 kJ/mol

B. Enthalpy of dissociation (ionization) of NH_4OH is 4.5 kJ/mol

C. Enthalpy of dissociation of CH_3COOH is 4.6 kJ/mol

D. ΔH for $2H_2O(l) \rightarrow 2H^+(aq.) + 2OH^-(aq.)$ is 114 kJ

Answer: A::B::D

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8. From the following data at $25^\circ C$

Reaction	$\Delta_r H^\circ$ kJ/mol
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$	-242
$H_2(g) \rightarrow 2H(g)$	436
$O_2(g) \rightarrow 2O(g)$	495

Which of the following statement (s) is/are correct:

A. $\Delta_r H^\circ$ for the reaction $H_2O(g) \rightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

B. $\Delta_r H^\circ$ for the reaction $OH(g) \rightarrow H(g) + O(g)$ is 502 kJ/mol

C. Enthalpy of formation of $H(g)$ is -218 kJ/mol

D. Enthalpy of formation of $OH(g)$ is 42 kJ/mol

Answer: A::D

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9. Which of the following do(es) not represent ΔH formation of the product.

A. $\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \rightarrow HBr$

B. $H_2(g) + Cl_2(g) \rightarrow 2HCl$

C. $NH_4^+(g) + Cl^-(g) \rightarrow NH_4Cl(s)$

D. $P_4(\text{black}) + 5O_2(g) \rightarrow P_4O_{10}(s)$

Answer: A::B::C::D

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10. From the following data, mark the option (s) where ΔH is correctly written for the given reaction. Given:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l) \quad \Delta H = -57.3kJ$

$\Delta H_{\text{solution}}$ of $HA(g) = -70.7$ kJ/mol

Δ_{solution} of $BOH(g) = 20$ kJ/mol

$\Delta H_{\text{ionization}}$ of $HA = 15$ kJ/mol & BOH is a strong base

A.

Reaction	ΔH_R (kJ/mole)
$HA(aq) + BOH(aq) \rightarrow BA(aq) + H_2O$	-42.3

B.

Reaction	ΔH_R (kJ/mole)
$HA(g) + BOH(g) \rightarrow BA(aq) + H_2O$	-93

C.

Reaction	ΔH_R (kJ/mole)
$HA(g) \rightarrow H^+(aq) + A^-(aq)$	-55.7

D.

Reaction	ΔH_R (kJ/mole)
$B^+(aq) + OH^-(aq) \rightarrow BOH(aq)$	-20

Answer: A::B::C

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11. Match the column-

	Column-I	Colum (ΔH_r
(A)	$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	(P)
(B)	$C(\text{graphite}) \rightarrow C(\text{gas})$	(Q)
(C)	$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$	(R)
		(S)

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12. Carafully observe the given diagrams which indicates standard enthalpy of formation of different states of one mole Mg and 2 mole Cl

atom and match the entries in column I and II provided.

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Exercise 3

1. When 2 moles of $C_2H_6(g)$ are completely burnt 3120 kJ of heat is liberated. Calculate the enthyalpy of formation, of $C_2H_6(g)$. Given $\Delta_f H$ for $CO_2(g)$ & $H_2O(l)$ are -395 & -286 kJ respectively.

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2. Calculate standard enthalpies of formation of carbon-di -sulphide (l). Given the standard enthylpy of combustion of carbon (s), sulphur (s) & carbon-di-sulphide (l) are :- 393.3, -293.72 and $-1108.76 kJ mol^{-1}$ respectively.

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3. From the following data at $25^{\circ}C$, Calculate the standard enthalpy of formation of $FeO(s)$ and of $Fe_2O_3(s)$.

	Reaction	$\Delta_r H^{\circ}$ (kJ/mole)
(1)	$Fe_2O_3(s) + 3C(\text{graphite}) \rightarrow 2Fe(s) + 3CO(g)$	492.6
(2)	$FeO(s) + C(\text{graphite}) \rightarrow Fe(s) + CO(g)$	155.8
(3)	$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$	-393.51
(4)	$CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$	-282.98

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4. The enthalpy change for the reaction $C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$ at $25^{\circ}C$ is -55.7 kJ/mol. Calculate the enthalpy of combustion of $C_2H_6(g)$. The enthalpy of combustion of H_2, & CH_4 are -285.8 & -890.0 kJ/mol respectively. enthalpy of combustion of propane is $-2220 \text{ kJ mol}^{-1}$.

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5. At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s), CO_2(g)$ & $H_2O(l)$ are , $-408, -393$ & $-286 \ \text{kJ mol}^{-1}$ respectively.

Calculate the heat of combustion of benzoic acid at :

(i) constant pressure

(ii) constant volume.

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6. A cylinder of gas is assumed to contains 11.2 kg of butane. If a normal family needs 20, 000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of conbustion, $\Delta H = -2658 \ \text{kJ/mole}$ for butane.

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7. Using bond enthalpy data, calculate enthalpy of formation of isoprene. Neglect resonance in isoprene.

$$5C(s) + 4H_2(g) \rightarrow H_2C = \underset{|}{\overset{|}{C}} - \underset{|}{\overset{|}{C}} = CH_2(g)$$
$$CH_3H$$

(Given :, $C - H = 98.9$ k Cal, , , $H - H = 104$ k Cal, ,), (, $C - C = 83$

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8. The heat of atomisation of $PH_3(g)$ and $P_2H_4(g)$ are $954kJmol^{-1}$ and $1485kJmol^{-1}$ respectively. The $P - P$ bond energy in $kJmol^{-1}$ is

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9. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

(Bond, $C - C, C = C, C - H, H - H$), (Bond Enthalpy, 336.81 kJ/mol,

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10. From the following data :

Enthalpy of formation of CH_3CN=87.86 kJ/mol

Enthalpy of formation of $C_2H_6 = -$ 83.68 kJ/mol

Enthalpy of sublimation of graphite =719.65 kJ/mol

enthalpy of dissociation of nitrogen =945.58 kJ/mol

Enthalpy of dissociation of $H_2 =$ 435.14 kJ/mol

$C - H$ bond enthalpy =414.22 kJ/mol

Calculate the bond enthalpy of (i) $C - C$, (ii) $C \equiv N$

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11. the enthalpy of combustion of acetylene is -312 kCal per mole. If enthalpy of formation of CO_2 & H_2O are -94.38 & -68.38 kCal per mole respectively, calculate $C \equiv C$ bond enthalpy.

given that enthalpy of atomisation of C is 150 kCal per mole and $H - H$ bond enthlpy and $C - H$ bond enthalpy are 103 kcal per mole and 93.64 kCal per mole respectively.

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12. Using the given data calculate enthalpy of formation of acetone (g).

[All value in $\mathrm{KJ\ mol^{-1}}$] bond enthalpy of :

$(C-H=413.4,,,C-C=347.0,,,(C=O)=728.0,,),((O=O)=$

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13. Find the enthalpy of $S-S$ bond from the following data.

$(i)\quad C_2H_5-S-C_2H_5(g)\qquad \Delta_f H^\circ = -147.2\ \mathrm{kJ/mol}$

$(ii)\quad C_2H_5-S-S-C_2H_5(g)\qquad \Delta_f H^\circ = -201.9\ \mathrm{kJ/mol}$

$(iii)\quad S(g)\qquad \Delta_f H^\circ = 222.8\ \mathrm{kJ/mol}$

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14. Calculate the enthalpy change when infinitely solution of $CaCl_2$ and Na_2CO_3 are mixed $\Delta_f H^\circ$ for $Ca^{2+}(aq, CO_3^{2-}(aq)$ and $CaCO_3(s)$ are $-129.80,\ -161.65,\ -288.5\ \mathrm{kCal\ mol^{-1}}$ respectively.

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15. The enthalpies of neutralization of $NaOH$ & NH_4OH by HCl are -13680 Cal and -12270 Cal respectively. What would be the enthalpy change if one gram equivalent of $NaOH$ is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and $NaCl$ are quantitatively obtained.

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16. The heat of solution of anhydrous $CuSO_4$ is -15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. The heat of hydration of $CuSO_4$ will be

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17. Determine ΔH for the following reaction at 500 K and constant pressure :

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$

Use the following data :

Substance	C_P (J/mol K)	$\Delta_f H(298K)$(kJ/mol)
CO	29.12	-110.5
H_2O	33.58	-241.8
CO_2	37.11	-393.5
H_2	29.89	0.0

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18. If the enthalpy of formation of $HCl(g)$ and $Cl^-(aq)$ are -92.3 kJ/mole and -167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

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19. From the data of ΔH of the following reactions

$C(s) + 1/2O_2(g) \rightarrow CO(g), \Delta H = -110kJ$

and $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g), \Delta H = 132kJ$

Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.

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20. 0.16 g of methane was subjected to combustion at $27^{\circ}C$ in a bomb calorimeter. The temperature of Calorimeter system (including water) was found to rise by $0.5^{\circ}C$. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure.

The thermal capacity of Calorimater system is $17.7\ \text{kJ K}^{-1}$. $\left(R = 8.313\ \text{J mol}^{-1}K^{-1}\right)$

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21. 1.0litre sample of a mixture of CH_4 and O_2 measured at $25^{\circ}C$ and 740 torr, was allowed to react at constant pressure in a calorimeter, together with its contents had a heat capacity of $1260 cal K^{-1}$. The complete combustion of CH_4 to CO_2 and water caused a temperature rise in calorimeter of $0.667K$. Calculate mole $\%$ of CH_4 in the original mixture. Heat of combustion of CH_4 is $-210.8 kcal$.

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22. Two solutions initially at $25^{\circ}C$ were mixed in an adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to $26.2^{\circ}C$. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution $1.0g/cm^3$, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the Calorimeter.

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23. Benzoic acid is a common standard used in Bomb calorimaters, which maintain a constant volume. If 1.2 gm of benzoic acid gives off 31.723 J of energy when burned in the presence of excess oxygen at an initial temperature of $24.6^{\circ}C$, calculate heat capacity at constant volume of final product mixture if final temperature is $47.34^{\circ}C$. Also calculate, W and ΔU for the given amount, assuming ideal gas behaviour.

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24. Calculate the electron gain enthalpy of fluorine atom using the following data. Make Born-Haber's cycle. All the values are in kJ mol^{-1} at $25^{\circ}C$.

$\Delta H_{\text{diss}}(F_2) = 160, \Delta_f H(NaF(s)) = -571, I.E.[Na(g)] = 494, \Delta H_{\text{sub}}[$

. Lattice enthalpy of $NaF(s) = 894$.

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25. The Born -Haber cycle for formation of rubidium chloride $(RbCl)$ is given below

(the enthalpies are in $KCalmol^{-1}$)

Find the value of X.

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26. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are -2839.2, -2275.2 and $-5506\ \text{kJ mol}^{-1}$ respectively. Calculate the resonance energy of benzene. The bond enthalpy of $C-H$ bond is given as equal to +410.87 kJ/mol.

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27. Calculate the enthalpy of combustion of methyl alcohol at 298 K from the following data

Bond	$C-H$	$C-O$	$O-H$	$O=O$	$C=O$
Bond Enthalpy $\left(kJmol^{-1}\right)$	414	351.5	464.5	494	711

Resonance energy of $CO_2 = -143\ \text{kJ mol}^{-1}$

Latent heat of vaporisation of methyl alcohol $= 35.5\ \text{kJ mol}^{-1}$

Latent heat of vaporisation of water $= 40.6\ \text{kJ mol}^{-1}$.

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28. Using the data given below, establish that the vapourisation of $CCl_4(l)$ at 298 K to produce $CCl_4(g)$ at 1 atm pressue does not occur spontaneously.

$\left(\text{Given :, } CCl_4(l, 1atm) \rightarrow CCl_4(g, 1atm), , , \Delta S^\circ = 94.98 \text{ JK}^{-1}mol^{-1}\right.$

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29. From the given table answer the following question:

	$CO(g)$	$CO_2(g)$	$H_2O(g)$	$H_2(g)$
$\Delta H^\circ_{298}(-\text{KCal/mole})$	-26.42	-94.05	-57.8	0
$\Delta H^\circ_{298}(-\text{KCal/mole})$	-32.79	-94.24	-54.64	0
$S^\circ_{298}(-\text{Cal/k mol})$	47.3	51.1	?	31.2

Reaction: $H_2O(g) + CO(g) \Leftrightarrow H_2(g) + CO_2(g)$

Calculate $S^\circ_{298}[H_2O(g)]$

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30. At temperature above 85 K, decarboxylation of acetic acid becomes a spontaneous process under standard state conditions. What is the

standard entropy change (in J/K-mol) of the reaction.

$$CH_3COOH(aq) \rightarrow CH_4(g) + CO_2(g)$$

$$\begin{aligned} \text{Given}: \quad \Delta H_f^\circ [CH_3COOH(aq)] &= -484 \ \text{kJ/mole} \\ \Delta H_f^\circ [CO_2(g)] &= -392 \ \text{kJ/mole} \\ \Delta H_f^\circ [CH_4(g)] &= -75 \ \text{kJ/mole} \end{aligned}$$

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31. By using the following data draw an appropriate enthalpy cycle & Calculate the enthalpy change of hydration of (i) the chloride ion , (ii) the iodide ion.

Comment on the difference in their values.

* enthalpy change of solution of $NaCl(s) = -2$ kJ/mol.
* enthalpy change of solution of $NaI(s) = +2$ kJ/mol.
* enthalpy change of hydration of $Na^+(g) = -390$ kJ/mol.
* lattice anthalpy of $NaCl = -772$ kJ/mol.
* lattice enthalpy of $NaI = -699$ kJ/mol.

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32. Calculate the heat produced when 3.785 litre of actane (C_8H_{18}) reacts with oxygen to form CO & water vapour at $25^\circ C$. The density of octane is 0.7025 gm/ml. enthalpy of combustion of C_8H_{18} is -1302.7 k Cal/mol.

$\left(\Delta H_f^\circ CO_2(g) = -94.05 \text{ k Cal mol}^{-1}, , , \Delta H_f^\circ CO(g) = -26.41 \text{ k Cal}\right.$

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33. Calculate the enthalpy of combustion of benzene (l) on the basis of the following data:

a. Resonance energy of benzene $(l) = -152kJ/mol$

b. Enthalpy of hydrogenation of cyclohexene $(l) = -119kJ/mol$

c. $\Delta_f H^\Theta C_6H_{12}(l) = -156kJmol^{-1}$

d. $\Delta_f H^\Theta ofH_2O(l) = -285.8kJmol^{-1}$

e. $\Delta_f H^\Theta ofCO_2(g) = -393.5kJmol^{-1}$

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34. The enthalpy of formation of $C_2H_5OH(l)$ is $-66kCal/mol$. The enthalpy of combustion of CH_3-O-CH_3 is $-348kCal/mol$. Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are $-94kCal/mol$ & $-68kCal/mol$ respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are all $25^\circ C$.

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35. A person takes 15 breaths per minute. The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume. The exhaled air contains 16% of oxygen by volume. If all the oxygen is used in the combustion of sucrose, how much of the Sucrose is burnt in the body per day & how much heat is evolved. ΔH_{com} of sucrose is $=6000kJmol^{-1}$. Take temperature to be 300 K throughout. [Assuming $V_{\text{inhaled air}}=V_{\text{exhalded air}}, P_{atm}=1atm$]

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36. The standard enthalpy of combustion of sucrose is $-5645 kJmol^{-1}$. What is the advantage (in $kJmol^{-1}$ of energy released as heat) of complete aerobic oxidation compared to anaerobic hydrolysis of sucrose to lactic acid ? ΔH_f° for lactic acid, CO_2 and H_2O is -694, -395.0 and -286.0 respectively.

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37. The enthalpies of neutralization of a weak acid HA & a weak acid HB by $NaOH$ are -6900 Cal/equivalent & -2900 Cal/equivalent repsectively. When one equivalent of NaOH is added to a solution containing one equivalent of HB, the enthalpy change was -3900 Calories. In what ratio is the base distribute between HA & HB ?

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38. Calculate the mass of mercury which can be liberated from HgO at $25^\circ C$ by the treatment of excess HgO with 41.84 kJ of heat at : (a)

constant pressure (b) constant volume

Given : $\Delta H_f^{\circ}(HgO, s) = -90.8 kJ mol^{-1}$ & $M(Hg) = 200.6 g mol^{-1}$.

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39. An intimate mixture of ferric oxide and aluminium is used as solid fuel in rockets. Calculate the fuel value per cm^3 of the mixture. Heats of formation and densities are as follows:

$H_{f(Al_2O_3)} = -399 kcal \quad mol^{-1}, H_{f(Fe_2O_3)} = -199 kcal \quad mol^{-1}$

ltbr. Density of $Fe_2O_3 = 5.2 g/cm^3$, Density of $Al = 2.7 g/cm^3$

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40. Calculate the enthalpy change for the following reaction:

$XeF_4 \rightarrow Xe^{\oplus} + F^{\Theta} + F_2 + F$. The average $Xe - F$ bond energy is $34 kcal mol^{-1}$, first IE of Xe is $279 kcal mol^{-1}$, EA of F is $85 kcal mol^{-1}$ and bond dissociation enegry of F_2 is $38 kcal mol^{-1}$

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41. During one of his adventure Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous and contains CO in addition to O_2 and N_2. Sabu, being huge, could not enter cave. In order to save Chacha Chaudhary he started sucking the poisonous air out of the cave by mouth. In each cycle he used to fill his lungs with cave air and exhale it out in the surroundings. In the mean time fresh air $(N_2 + O_2)$ from the surrounding effused into cave till the pressure was 1 atmosphere. Each time Sabu sucked air,the pressure in the cave dropped ito $1/2atm$. An initial sample of air taken from the cave measured $11.2mL$ at STP and give $7J$ on complete combusion at constant pressure.

(a) If the safe level of CO required in cave for life is less thatn $0.001\,\%$ by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary ?

(b) Sabu should rescue Chacha Chaudhary within 10 minutes else he will die. Precious 80 second are wasted in thinking of a way to rescue him. At maximum how much time should each cycle of inhaling $-$ exhaling take.

Given, $\Delta H_{comb}CO = -280kJmol^{-1}$? Neglect Graham's law effect during operations.

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42. For an ionic solid MX_2, where X is monovalent, the enthalpy of formation of the enthalpy of formation of the solid from M (s) and $X_2(g)$ is 1.5 times the electron gain enthalpy of $X(g)$. The first and second ionisation enthalpies of the meta (M) are 1.2 and 2.8 times of the enthalpy of sublimation of $M(s)$. The bond dissociation enthalpy of $X_2(g)$ is 0.8 times the first ionisation enthalpy of metal and it is also equal to one - fifth of the magnitude of lattice enthalpy of MX_2. If the electron gain enthalpy of $X(g)$ is $-96Kcal/mol$, the answer the enthalpy of sublimation of metal (M) in K cal/mol

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Exercise 4

1. Which of the following is not an endothermic reaction?

A. Combustion of methane

B. Decomposition of water

C. Dehydrogenation of ethane to ethylene

D. Conversion of graphite to diamond

Answer: A

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2. Estimate the average $S-F$ bond enthalpy in SF_6. The values of standard enthalpy of formation of $SF_6(g)$, $S(g)$ and $F(g)$ are :-1100, 274 and $80kJmol^{-1}$ respectively.

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3. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

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

from the following data, the enthalpy change for the combustion of diborane will be :

$2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s), \qquad \Delta H = -1273 \text{ kJ}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \qquad \Delta H = -286 \text{ kJ}$

$H_2O(l) \rightarrow H_2O(g), \qquad \Delta H = 44 \text{ kJ}$

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g), \qquad \Delta H = 46 \text{ kJ}$

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4. ΔH_1° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are -393.5, -110.5 and $-241.8 kJmol^{-1}$ respectively. Standard enthalpy change for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is

A. 524.1

B. 41.2

C. -262.5

D. -41.2

Answer: B

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5. Which of the following reactions defines ΔH_f°?

A. $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g)$

B. $1/2H_2(g) + 1/2F_2(g) \rightarrow HF(g)$

C. $N_2(g) + 3H_2(g) \rightarrow 2NH_3$

D. $CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$

Answer: B

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6. 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 process. Given that the heat capacity of the calorimeter is was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is $2.5kJK^{-1}$, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

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7. The species which by definition has ZERO standard molar enthyalpy of formation at 298 K is

A. $Br_2(g)$

B. $Cl_2(g)$

C. $H_2O(g)$

D. $CH_4(g)$

Answer: B

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8. Match the transformation in column I with appropriate option in column II

	Column I		Column II
(A)	$CO_2(s) \rightarrow CO_2(g)$	(p)	phase transition
(B)	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	(q)	allotropic change
(C)	$2H^{\cdot} \rightarrow H_2(g)$	(r)	ΔH is positive
(D)	$P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$	(s)	ΔS is positive
		(t)	ΔS is negative

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9. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose (s) at $25^\circ C$ are -400 kJ/mol, -300 kJ/mol and -1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at $25^\circ C$ is :

A. $+2900kJ$

B. $-2900kJ$

C. $-16.11kJ$

D. $+16.11kJ$

Answer: C

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10. When 100 mL of $1.0MHCl$ was mixed with 100 mL of $0.1MNaOH$ in an insulated beaker at constant pressure, a temperature increase of $5.7^{\circ}C$ was measured for the beaker and its contents. Because the enthypy of neutralization of a strong acid with a strong base is a constant $\left(-57.0\ \text{kJ mol}^{-1}\right)$, this experiment could used to measure the calorimeter constant.

In a second experiment 100 mL of $2.0M$ acetic acid $\left(K_a = 2.0 \times 10^{-5}\right)$ was mixed with 100 mL of $1.0MNaOH$ (under identical conditions of Expt. 1) where a temperature rise of $5.6^{\circ}C$ was measured.

(Consider heat capacity of all solutions as $4.2Jg^{-1}K^{-1}$ and density of all solutions as $1.0gmL^{-1}$)

Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid from the Expt. 2 is

A. 1.0

B. 10.0

C. 24.5

D. 51.4

Answer: A

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11. When 100 mL of $1.0MHCl$ was mixed with 100 mL of $0.1MNaOH$ in an insulated beaker at constant pressure, a temperature increase of $5.7^{\circ}C$ was measured for the beaker and its contents. Because the enthypy of neutralization of a strong acid with a strong base is a constant $\left(-57.0\ \text{kJ mol}^{-1}\right)$, this experiment could used to measure the calorimeter constant.

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(Consider heat capacity of all solutions as $4.2Jg^{-1}K^{-1}$ and density of all solutions as $1.0gmL^{-1}$)

The pH of the solution after Expt. 2 is

A. 2.8

B. 4.7

C. 5.0

D. 7.0

Answer: B

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12. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below :

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{\text{diss}}H^{\Theta}} Cl(g) \xrightarrow{\Delta_{eg}H^{\Theta}} Cl^-(g) \xrightarrow{\Delta_{\text{hyd}}H^{\Theta}} Cl^-(aq)$$

The energy involved in the conversion of $\frac{1}{2}Cl_2(g)$ to $Cl^-(aq)$ (using the data,

$\Delta_{\text{diss}} H^{\Theta}_{Cl_2} = 240 \text{ kJ mol}^{-1}$, $\Delta_{\text{eg}} H^{\Theta}_{Cl} = -349 \text{ kJ mol}^{-1}$, $\Delta_{\text{hyd}} H^{\Theta}_{Cl^-} = -$

) will be -

A. -610 kJ mol^{-1}

B. -850 kJ mol^{-1}

C. $+120 \text{ kJ mol}^{-1}$

D. $+152 \text{ kJ mol}^{-1}$

Answer: A

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13. Standard entropy of X_2, Y_2 and XY_3 are 60, 40 and 50 $\text{J K}^{-1} mol^{-1}$, respectively. For the reaction, $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3 \Delta H = -30kJ$, to be at equilibrium, the temperature will be

A. 500 K

B. 750 K

C. 1000 K

D. 1250 K

Answer: B

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14. On the basis of the following thermochemical data $\left(\Delta fG^{\circ}H^{+}_{(aq)} = 0\right)$

$H_2O(l) \rightarrow H^{+}(aq) + OH^{-}(aq), \Delta H = 57.32kJ$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta H = -286.20kJ$

The value of enthalpy of formation of OH^{-} ion at $25^{\circ}C$ is -

A. $-228.88kJ$

B. $+228.88kJ$

C. $-343.52kJ$

D. $-22.88kJ$

Answer: A

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15. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is $CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ at $298K$ standard Gibb's energies of formation for $CH_3OH(l)$, $H_2O(l)$ and $CO_2(g)$ are $-166.2,\ -237.2$ and $-394.4\ \text{kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is $-726\ \text{kJ mol}^{-1}$, efficiency of the fuel cell will be -

A. $87\ \%$

B. $90\ \%$

C. $97\ \%$

D. $80\ \%$

Answer: C

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