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CHEMISTRY

TARGET : JEE Advanced - 2021

CAPS – 20

Thermodynamics

Answer Key

1.	(C)	**2.**	(C)	**3.**	(B)	**4.**	(B)	**5.**	(A)
6.	(D)	**7.**	(C)	**8.**	(D)	**9.**	(D)	**10.**	(A)
11.	(B)	**12.**	(A)	**13.**	(ACD)	**14.**	(BCD)	**15.**	(AC)
16.	(C)	**17.**	(A)	**18.**	(D)	**19.**	(C)	**20.**	(D)
21.	(A)	**22.**	(C)	**23.**	(B)				

Solution

SINGLE CHOICE QUESTIONS

1. A heating coil is immersed in a 100 g sample of $H_2O(l)$ at 1 bar and 100ºC in a closed vessel. In this heating process, 60% of the liquid is converted into gaseous form at constant pressure of 1 bar. Densities of liquid and gaseous water under these conditions are 1000 kg/m^3 and 0.60 kg/m^3 respectively. Magnitude of the work done for the process is:

(A) 4997 K (B) 4970 J (C) 9994 J (D) None of these

Ans. **(C)**

Sol. $w = -P_{ext}(V_f - V_i)$

$= -10^5\left(\frac{60\times10^{-3}}{0.60}+\frac{40\times10^{-3}}{1000}-\frac{100\times10^{-3}}{1000}\right)$

$= -10^5(100 \times 10^{-3} + 0.04 \times 10^{-3} - 0.1 \times 10^{-3})$

$|w| = 9994$ J

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

$H_2O\ (l, 323\ K) \rightarrow H_2O\ (g, 423\ K)$

Given: $C_{v,m}$ (H_2O, l) = 75.0 JK^{-1} mol^{-1}; $C_{p,m}$ (H_2O, g) = 33.314 JK^{-1} mol^{-1}

ΔH_{vap} at 373 K = 40.7 kJ/mol

(A) 42.91 kJ/mol (B) 43086 kJ/mol (C) 42.6 kJ/mol (D) 49.6 kJ/mol

Ans. **(C)**

Sol. $H_2O(1,323K)\xrightarrow{\Delta U_1}H_2O(1,373K)\xrightarrow{\Delta U_2}H_2O(g,373K)\xrightarrow{\Delta U_3}H_2O(g,323K)$

CV,m(H_2O,g) = 33.314 − 8.314

= 25 J/Kmol

$\Delta U_2 = \Delta H_2 - \Delta ngRT = 37.6$

$\Delta U_{total} = DU_1 + \Delta U_2 + \Delta U_3$

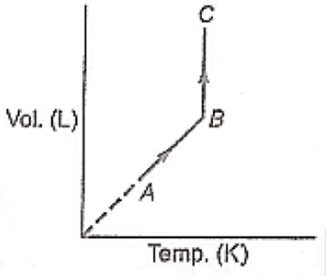
$= C_{V,m}(l).\Delta T + \Delta V_{vap.} + C_{v,m}(g)\Delta T$

$= \frac{75\times50}{1000}+37.6+\frac{25\times50}{1000}$

= 42.6 kJ/mol

3. Two moles of a triatomic linear gas (neglect vibration degree of freedom) are taken through a reversible process ideal starting from A as shown in figure.

The volume ratio $\frac{V_B}{V_A} = 4$. If the temperature at A is –73ºC, then:



Total enthalpies change in both steps is:

(A) 3000 R (B) 4200 R (C) 2100 R (D) 0

Ans. **(B)**

Sol. $\Delta H_{total} = \Delta H_{AB} + \Delta H_{BC} = nC_{p,m}\,\Delta T + 0$

$= 2 \times \frac{7}{2} \times R \times (800 - 200)$

$= 4200R$

4. For polytropic process PV^n = constant, molar heat capacity (C_m) of an ideal gas is given by

(A) $C_{v,m} + \frac{R}{(n-1)}$ (B) $C_{v,m} + \frac{R}{(1-n)}$ (C) $C_{v,m} + R$ (D) $C_{p,m} + R\frac{R}{(n-1)}$

Ans. **(B)**

Sol. $dU = dq + dw$

$nC_{v,m}.\ dT = nC_m.\ dT - P.dV$

$C_m = C_{v,m} + \frac{P.dV}{n.dT}$ .....(1)

$PV^n = K and PV = nRT$

$\therefore$ $KV^{1-n} = nRT$

$K(1-n)V^{-n}.\ dV = nRdT$

$\frac{dV}{dT} = \frac{nR}{K(1-n)V^{-n}}$ .....(2)

From Equations (1) and (2)

$C_m = C_{v,m} + \frac{R}{(1-n)}$

5. One mole of an ideal monoatomic gas at 27oC is subjected to a reversible iso-entropic compression until final temperature reaches to 327oC. If the initial pressure as 1.0 atm then find the value of (ln P_2): (Given: ln 2 = 0.7)

(A) 1.75 atm (B) 0.176 atm (C) 1.0395 atm (D) 2.0 atm

Ans. **(A)**

Sol. For iso-entropic process $\Delta_{system} = 0$

$\therefore\ nC_{p,m}\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2} = 0 \quad \Rightarrow \quad \ln(P_2) = \frac{5}{2} \times \ln\left(\frac{600}{300}\right)$

= 1.75 atm

6. Using listed information's, calculate ΔrG^o (in kJ/mol) at 27ºC

	$Co_3O_4(s)$ +	$4CO(g) \rightarrow$	$3Co(s)$ +	$4CO_2(g)$
Given: At 300 K	ΔH^o_f (kJ/mol) –891,	–110.5,	0.0,	–393.5
	S^o (J/K-mol) 102.5,	197.7,	30.0,	213.7

(A) –214.8 (B) –195.0 (C) –200.3 (D) –256.45

Ans. **(D)**

Sol. $\Delta_r H^o = 3.\Delta_f H^o(CO,s) + 4\Delta_f H^o(CO_2,g)$

$-\Delta_f H^o(Co_3O_4,s) - 4.\Delta_f H^o(CO,g)$

$\Delta_r S^o = 3 \times 30 + 4 \times 213.7 - 102.5 - 4 \times 197.7$

= 51.5 J/K-mol

$\therefore \Delta_r G^o = \Delta_r H^o - T.\Delta_r S^o$

$= -241 - \frac{300 \times 51.5}{1000}$

= −256.45 kJ/mol

7. Consider the following data:

$\Delta fHo\ (N_2H_4, l) = 50$ kJ/mol, $\Delta_f H^o\ (NH_3, g) = -46$ kJ/mol

B.E. (N–H) = 393 kJ/mol and B.E. (H–H) = 436 kJ/mol

$\Delta_{vap}H\ (N_2H_4, l) = 18$ kJ/mol

The N–N bond energy in N_2H_4 is:

(A) 226 kJ/mol (B) 154 kJ/mol (C) 190 kJ/mol (D) None of these

Ans. **(C)**

Sol. $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$

Let B.E. of N ≡ N is x

$= 46 = \frac{x}{2} + \frac{3}{2} \times 436 - 3 \times 393 \Rightarrow x = 958$

$N_2H4(l) \rightarrow N_2(g) + 2H_2(g)$;

= –50 kJ/mol

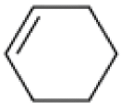
$$\Delta_r H = \begin{bmatrix} \Delta_{vap}H(N_2H_4,l) \\ +4 \times B.E.(N-H) \\ +B.E.(N-N) \end{bmatrix} - \begin{pmatrix} B.E.(N \equiv N) \\ +2B.E.(H-H) \end{pmatrix}$$

$-50 = (18 + 4 \times 393 + y) - (958 + 2 \times 436)$

$-50 = (1590 + y) - (1830)$

B.E. (N – N) or y = 190 kJ/mol

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



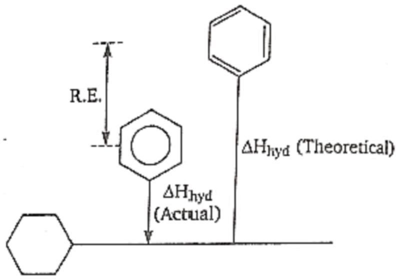
is Assume ΔH_{vap} of $C_6H_6(l)$, $C_6H_8(l)$, $C_6H_{12}(l)$ all are equal:

(A) –535.5 kJ/mol (B) –238 kJ/mol (C) –357 kJ/mol (D) –119 kJ/mol

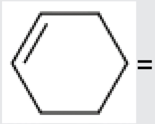
Ans. **(D)**

Sol. Theoretical heat of hydrogenation of benzene

= (Actual heat of hydrogenation) + (Resonance energy)



$= -205 - 152 = -357$

Enthalpy of hydrogenation of  $= \frac{-357}{3} = -119\text{kJ/mol}$

9. For the reaction taking place at certain temperature

$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$,

if equilibrium pressure is 3X bar then $\Delta_r G^o$ would be

(A) $-RT \ln 9 - 3RT \ln X$ (B) $RT \ln 4 - 3RT \ln X$

(C) $-3RT \ln X$ (D) None of these

Ans. **(D)**

Sol. $\Delta G^o = -RT \ln K_p$; $K_p = (2x)^2 X = 4X^3$

$\Delta G^o = -RT \ln(4X^3)$

$\Delta G^o = -RT \ln 4 - 3\,RT \ln X$

10. Gibbs Helmholtz equation relates the enthalpy, entropy and free energy change of the process at constant pressure and temperature as

$\Delta G = \Delta H - T\Delta S$ (at constant P, T)

In general, the magnitude of ΔH does not change much with the change in temperature but the term $T\Delta S$ changes appreciably. Hence in some process spontaneity is very much dependent on temperature and such processes are generally known as entropy driven process.

For the reaction at 298 K; $A_2B_4 \rightarrow 2AB_2$

$\Delta H = 2\text{kJ}$ and $\Delta S = 20$ J/K at constant P and T, the reaction will be

(A) spontaneous and entropy driven (B) spontaneous and enthalpy driven

(C) non-spontaneous (D) at equilibrium

Ans. **(A)**

Sol. $(\Delta G)_{PT} = 2000 - (20 \times 298) = -3960\text{J/mol}$

11. Gibbs Helmholtz equation relates the enthalpy, entropy and free energy change of the process at constant pressure and temperature as

$\Delta G = \Delta H - T\Delta S$ (at constant P, T)

In general the magnitude of ΔH does not change much with the change in temperature but the term $T\Delta S$ changes appreciably. Hence in some process spontaneity is very much dependent on temperature and such processes are generally known as entropy driven process.

When $CaCO_3$ is heated to a high temperature it decomposes into CaO and CO_2, however it is quite stable at room temperature. It can be explained by the fact that

(A) ΔrH dominates the term $T\Delta S$ at high temperature

(B) the term $T\Delta S$ dominates the ΔrH becomes negative

(C) at high temperature both ΔrS and ΔrH becomes negative

(D) thermodynamics can not say anything about spontaneity

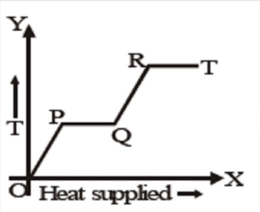
Ans. **(B)**

Sol. $CaCO_3 \rightarrow CaO + CO_2$ ΔH + ve

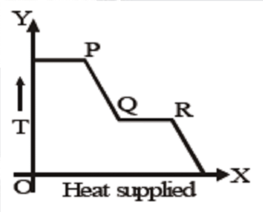
Reaction becomes spontaneous at high temperature because $T\Delta S$ dominates over ΔH_{rxn}

12. A block of ice at –10°C is slowly heated and converted into steam at 100°C. Which of the following curves represents the phenomenon qualitatively?

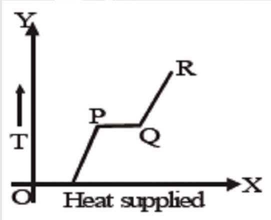
(A)



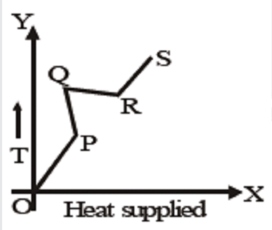
(B)



(C)



(D)



Ans. **(A)**

Sol. During phase changes, the temperature remains constant.

MULTIPLE CHOICE QUESTIONS

13. When ice melts at 1ºC:

(A) an increase in entropy

(B) a decrease in enthalpy

(C) a decrease in free energy

(D) process is spontaneous

Ans. **(ACD)**

Sol. Entropy ↑ intermolecular force ↓

$\Delta H > 0$

Spontaneous process $\Delta G = 0$

14. The value of $\Delta H_{transition}$ of C (graphite) → C (diamond) is 1.9 kJ/mol at 25oC. Entropy of graphite is higher than entropy of diamond. This implies that:

(A) C (diamond) is more thermodynamically stable than C (graphite) at 25ºC

(B) C (graphite) is more thermodynamically stable than C (diamond) at 25ºC

(C) diamond will provide more heat on complete combustion at 25ºC

(D) ΔGtransition of C (diamond) ⟶ C(graphite) is –ve

Ans. **(BCD)**

Sol. C(graphite) → C(diamond)

$\Delta G = \Delta H - T\Delta S = 1.9 - 298(-ve) = +ve$

Graphite is more stable than diamond thermodynamically

$\Delta_r H = (\Delta_C H)_G - (\Delta CH)_D,\ (\Delta CH)_G = -x\ (\Delta_C H)_D = -y$

$1.9 = -x + y \Rightarrow y = 1.9 + x$

Diamond provides more heat on complete combustion in comparison of graphite

15. For an isolated system, the entropy:

(A) either increases or remains constant

(B) either decreases or remains constant

(C) can never decrease

(D) can never increase

Ans. **(AC)**

Sol. Entropy of isolated system increases or remains constant, but it can never decrease.

COMPREHENSION # 1 (FOR Q. 16 TO Q.20)

Standard Gibb's energy of reaction ($\Delta_r G^o$) at a certain temperature can be computed as $_{\Delta r}G^o = \Delta_r H^o - T.\Delta_r S^o$ and the change in the value of $\Delta_r H^o$ and $\Delta_r S^o$ for a reaction with temperature can be computed as follows:

$$\Delta_r H^o T_2 - \Delta_r H^o_{T_1} = \Delta_r C^o_P (T_2 - T_1)$$

$$\Delta_r S^o_{T_2} - \Delta_r S^o_{T_1} = \Delta_r C^o_P \ln\left(\frac{T_2}{T_!}\right)$$

$\Delta_r G^o = \Delta_r H^o - T\ .\ \Delta_r S^o$

and by $\Delta_r G^o = -RT \ln K_{eq}$.

Consider the following reaction:

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Given: $\Delta_f H^o$ (CH_3OH, g) = – 201 kJ/mol; $\Delta_f H^o$ (CO, g) = – 114 kJ/mol

S^o (CH_3OH, g) = 240 J/mol-K; S^o (H_2, g) = 29 $JK^{-1}\ mol^{-1}$

S^o (CO, g) = 198 J/mol-K; $C^o_{p,\,m}$ (H_2) = 28.8 $JK^{-1}\ mol^{-1}$

$C^o_{p,m}$ (CO) = 29.4 J/mol-K; $C^o_{p,m}$ (CH_3OH) = 44 J/mol-K

and $\ln\left(\frac{320}{300}\right) = 0.06$, all data at 300 K.

16. $\Delta_r S^o$ at 300 K for the reaction is:

(A) 152.6 J/K-mol (B) 181.6 J/K-mol (C) –16 J/K-mol (D) None of these

Ans. **(C)**

Sol. $CO + 2H2 \rightleftharpoons CH3OH$

$\Delta S^o = S^o(CH_3OH) - S^o(CO) - 2 \times S^o(H_2)$

$= 240 - 198 - (2 \times 29)$

$= 240 - 198 - 58$

$= -16$ J/K mol

17. $\Delta_r H^o$ at 300 K for the reaction is

(A) –87 kJ/mol (B) 87 kJ/mol (C) –315 kJ/mol (D) –288 kJ/mol

Ans. **(A)**

Sol. $CO + 2H2 \rightleftharpoons CH3OH$

$\Delta_r H = \Delta_f H(CH_3OH) - (2 \times \Delta_f H(H_2)) - \Delta_f H(CO)$

$= -201 - 0 - (-114)$

$= -87$ kJ/mol

18. $\Delta_r S^o$ at 320 K is

(A) 155.18 J/mol-K (B) 150.02 J/mol-K (C) 172 J/mol-K (D) None of these

Ans. **(D)**

Sol. $S_{320} = S^{\circ}_{320} + C_p \ln\frac{T_2}{T_1}$

For $CH_3OH \Rightarrow S_{320} = 240 + 44 \times 0.06 = 242.64$ J/K -Mol

For $H_2 \Rightarrow S_{320} = 29 + 28.8 \times 0.06 = 30.728$ J/K -Mol

For $CO \Rightarrow S_{320} = 198 + 29.4 \times 0.06 = 199.764$ J/K -Mol

Now,

$\Delta_r S_{320} = S(CH_3OH) - (2 \times S(H_2) - S(CO)$

$= 242.64 - (2 \times 30.728) - 199.764$

$= 242.64 - 61.456 - 199.764$

$= -18.58$ J/K -mol

19. $\Delta_r H^o$ at 320 K is

(A) –288.86 kJ/mol (B) –289.1 kJ/mol (C) –87.86 kJ/mol (D) None of these

Ans. **(C)**

Sol. $\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$

$\Rightarrow \Delta H_{320} = \Delta H_{300} + (44-(2\times28.8)-29.4)(320-300)\times10^{-3}$

$= -87 + \frac{(-43)\times 20}{1000}$

$= -87 - 0.86$

$= -87.86$ kJ/ mol

20. $\Delta_r G^o$ at 320 K is

(A) –48295.2 kJ/mol (B) –240.85 kJ/mol (C) 240.85 kJ/mol (D) –81.91 kJ/mol

Ans. **(D)**

Sol. $\Delta G = \Delta H - T\Delta S$

$\Rightarrow \Delta G_{320} = -87.86 - 320 \times (-18.58) \times 10^{-3}$

$= -87.86 + 5.9456$

$= -81.9144$ kJ/ mol

MATRIX TYPE QUESTIONS

21. Column I and Column II contains four entries each. Entries of Column I are to be matched with some entries of column II. One or more than one entries of Column I may have the matching with the same entries of Column II.

Column-I (Process)	**Column-II (Entropy Change)**
(A) Reversible isothermal compression of an ideal gas	(P) ΔSSystem > 0
(B) Isothermal free expansion (Pext = 0) of an ideal gas	(Q) ΔSSystem < 0
(C) Reversible adiabatic expansion of an ideal gas	(R) ΔSSystem = 0
(D) Reversible ideal gas expansion	(S) Information insufficient

(A) A → Q; B → P; C → R; D → S (B) A → Q; B → P, S; C → P; D → R

(C) A → R; B → Q; C → Q; D → P, S (D) A → S; B → P, R; C → Q; D → P, R

Ans. **(A)**

Sol. Fact

22. Match the following

Column-I	**Column-II**
(A) (ΔGsystem)T,P	(P) $nR\ln\left(\frac{V_2}{V_1}\right)$
(B) Work done in reversible isothermal ideal gas expansion	(Q) $nRT\ln\left(\frac{P_2}{P_1}\right)$
(C) ΔG for reversible isothermal expansion of an ideal gas	(R) −nFE
(D) ΔSgas for isothermal expansion of an ideal gas	(S) $nR\ln\left(\frac{P_1}{P_2}\right)$

(A) A → Q; B → P; C → R; D → S (B) A → Q; B → P, S; C → P; D → R

(C) A → R; B → Q; C → Q; D → P, S (D) A → S; B → P, R; C → Q; D → P, R

Ans. **(C)**

Sol. Fact

23. Match the following

Column-I	**Column-II**
(A) $\left(\frac{\partial U}{\partial T}\right)_V$	(P) CP
(B) $\left(\frac{\partial H}{\partial T}\right)_P$	(Q) CV
(C) $\left(\frac{\partial G}{\partial T}\right)_P$	(R) −S
(D) $\left(\frac{\partial G}{\partial P}\right)_T$	(S) V

(A) A → P, R; B → Q; C → P, R; D → Q, S (B) A → Q; B → P; C → R; D → S

(C) A → S; B → R; C → P; D → Q (D) A → S; B → P, R; C → Q; D → P, R

Ans. **(B)**

Sol. Fact

SUBJECTIVE ANSWER TYPE

24. One mole of an ideal monoatomic gas is carried through the cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3. Fill in the blank space in the table given below assuming reversible steps.

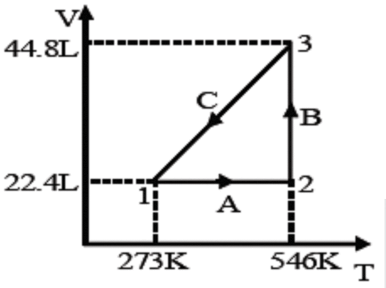


Table-1			
State	**P**	**V**	**T**
1			
2			
3			

Step	**Name of process**	**q**	**w**	ΔE	ΔH
A					
B					
C					
overall					

Sol.

Table-1			
State	**P**	**V**	**T**
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	**Name of process**	**q**	**w**	ΔE	ΔH
A	Isochoric	3/2 R(273)	0	3/ 2 R(273)	5/ 2 R (273)
B	Isothermal	546 R In 2	–546 R In 2	0	0
C	Isobaric	–5/ 2 R (273)	R (273)	–3/ 2 R(273)	–5/ 2 R (273)
overall	cyclic	546RIn2–273R	273R–546RIn2	0	0