


EXERCISE # (O-I)


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**Carnot cycle and 2<sup>nd</sup> law of thermodynamics**

- The maximum efficiency of a heat engine operating between 100°C and 25°C is :-  
(A) 20.11% (B) 22.2% (C) 25.17% (D) 30%
- A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :-  
(A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal
- A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360K. If the efficiencies of engines A and B are the same then the temperature  $T_2$  is :-  
(A) 680 K (B) 640 K (C) 600 K (D) 800 K

**Entropy calculation and  $\Delta S$**

- Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is :-  
(A)  $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$  (B)  $\Delta S_{\text{system}} > 0$  only  
(C)  $\Delta S_{\text{surroundings}} > 0$  only (D)  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
- 2 mole of ideal gas at 27°C temperature is expanded reversibly from 2 lit. to 20 lit. Find entropy change ( $R = 2 \text{ cal/mol K}$ ) :-  
(A) 92.1 (B) 0 (C) 4 (D) 9.2
- The entropy changes when two moles of ideal monoatomic gas are heated from 200 to 300° C reversibly and isochorically :-  
(A)  $\frac{3}{2} R \ln \left( \frac{300}{200} \right)$  (B)  $\frac{5}{2} R \ln \left( \frac{573}{273} \right)$  (C)  $3R \ln \left( \frac{573}{473} \right)$  (D)  $\frac{3}{2} R \ln \left( \frac{573}{473} \right)$
- When one mole of an ideal gas is compressed to half to its initial volume & simultaneously heated to twice its initial temperature. The change in entropy ( $\Delta S$ ) of gas is :  
(A)  $C_v \ln 2$  (B)  $C_p \ln 2$  (C)  $R \ln 2$  (D)  $(C_v - R) \ln 2$
- The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is :-  
(A) 1.385 cal/K (B) - 1.2 cal/K (C) 1.2 cal/K (D) 2.77 cal/K

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9. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ( $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ ) for given process.
- (A) 56 J/K                      (B) 14 J/K                      (C) 16 J/K                      (D) 20 J/K
10. An isobaric process having one mole of ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity ( $C_V$ ) ?
- (A)  $\frac{10}{\log 2}$  J/K mol                      (B)  $\frac{10}{\log 2} - 8.3$  J/K mol
- (C)  $10 \times \log 2$  J/K mol                      (D)  $10 \log 2 + 8.3$  J/K mol
11. When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by ?
- (A)  $C \ln \frac{T_c + T_h}{2T_c}$                       (B)  $C \ln \frac{T_2}{T_1}$                       (C)  $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$                       (D)  $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

### Entropy change for phase change

12. If  $\Delta H_{\text{vaporisation}}$  of substance X( $\ell$ ) (molar mass : 30 g/mol) is 300 J/g at it's boiling point 300 K, then molar entropy change for reversible condensation process is :-
- (A) 30 J/mol.K                      (B) -300 J/mol.K                      (C) -30 J/mol.K                      (D) 300 J/mol.K
13. For the liquid A whose normal boiling point is 300K,  $\Delta S_{\text{univ}}$  for the reaction at one atm and 300K is-
- $$A(l) \xrightarrow[300K]{1\text{atm}} A(g) ;$$
- $\Delta V_{\text{aporisation}} = 60\text{kJ} / \text{mol}$  at 1atm & 300K
- (A) zero
- (B) -2 J/mol-K
- (C) 200 J/mol-K
- (D) -200 J/mol-K

### Physical significance of entropy, disorder

14. When two gases are mixed the entropy :-
- (A) Remains constant                      (B) Decreases                      (C) Increases                      (D) Becomes zero

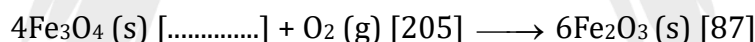
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15. For the process,  $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$  :
- (A) Both  $\Delta H$  and  $\Delta S$  are +ve (B)  $\Delta H$  is negative and  $\Delta S$  is +ve  
 (C)  $\Delta H$  is +ve and  $\Delta S$  is -ve (D) Both  $\Delta H$  and  $\Delta S$  are -ve
16.  $\Delta S$  for the reaction ;  $\text{MgCO}_3(\text{s}) \longrightarrow \text{MgO}(\text{s}) + \text{CO}_2(\text{g})$  will be :
- (A) 0 (B) -ve (C) +ve (D)  $\infty$
17. Change in entropy is negative for :-
- (A) Bromine ( $\ell$ )  $\longrightarrow$  Bromine (g)  
 (B)  $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$   
 (C)  $\text{N}_2(\text{g}, 10 \text{ atm}, 298 \text{ K}) \longrightarrow \text{N}_2(\text{g}, 1 \text{ atm}, 298 \text{ K})$   
 (D)  $\text{Fe}(\text{at } 400 \text{ K}) \longrightarrow \text{Fe}(\text{at } 300 \text{ K})$
18. For which reaction from the following,  $\Delta S$  will be maximum ?
- (A)  $\text{Ca}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CaO}(\text{s})$  (B)  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$   
 (C)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  (D)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
19. For conversion  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{Diamond})$ , the  $\Delta S$  is :-
- (A) Zero (B) Positive (C) Negative (D) Can not be predicted

### $\Delta S$ for chemical reaction

20. If  $S^\circ$  for  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 0.13, 0.22 and 0.19  $\text{KJ K}^{-1} \text{mol}^{-1}$  respectively. The total change in standard entropy for the reaction,  $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$  is :
- (A) 30  $\text{JK}^{-1} \text{mol}^{-1}$  (B) 40  $\text{JK}^{-1} \text{mol}^{-1}$  (C) 60  $\text{JK}^{-1} \text{mol}^{-1}$  (D) 20  $\text{JK}^{-1} \text{mol}^{-1}$
21. Given  $\Delta_r S^\circ = -266$  and the listed [ $S^\circ_m$  values].

Calculate  $S^\circ$  for  $\text{Fe}_3\text{O}_4(\text{s})$  :



- (A) +111.1 (B) +122.4 (C) 145.75 (D) 248.25

### Kirchoff's equation : Variation of $\Delta S$ and $\Delta H$ with Temperature


22. In Haber's process of manufacturing of ammonia :



Molecule	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$C_p \text{ JK}^{-1} \text{mol}^{-1}$	29.1	28.8	35.1

If  $C_p$  is independent of temperature, then reaction at  $100^\circ\text{C}$  as compared to that of  $25^\circ\text{C}$  will be :

- (A) More endothermic (B) Less endothermic  
 (C) More exothermic (D) Less exothermic

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23. Predict the standard enthalpy of the reaction  $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  at  $100^\circ\text{C}$ . If standard enthalpy of this reaction is  $-57.2 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ ? (Given  $C_p(\text{NO}_2) = 37.2 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $C_p(\text{N}_2\text{O}_4) = 77.28 \text{ J. mol}^{-1} \text{ K}^{-1}$ )  
(A)  $-56.98 \text{ J mole}^{-1}$  (B)  $-76.27 \text{ J mole}^{-1}$  (C)  $-54.23 \text{ J mole}^{-1}$  (D)  $-120 \text{ J mole}^{-1}$
24. Entropy change for  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{s})$  at 1 atm and  $-10^\circ\text{C}$ , is  
[Given :  $\Delta H_{\text{fusion}}(0^\circ\text{C}) = 6000 \text{ J/mol}$ ,

$$C_{p,m}(\text{H}_2\text{O}, \text{s}) = 36 \text{ J/K-mol}, C_{p,m}(\text{H}_2\text{O}, \text{l}) = 75 \text{ J/K-mol}, \ln\left(\frac{273}{263}\right) = 0.04$$

- (A)  $-23.47 \text{ J/K-mol}$   
(B)  $-20.41 \text{ J/K-mol}$   
(C)  $21 \text{ J/K-mol}$   
(D)  $20.47 \text{ J/K-mol}$

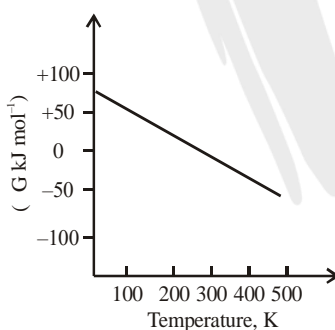
**Change in Gibb's free energy ( $\Delta G$ )**

25. Identify the correct statement for change of Gibbs energy for a system ( $\Delta G_{\text{system}}$ ) at constant temperature and pressure.  
(A) If  $\Delta G_{\text{system}} > 0$ , the process is spontaneous.  
(B) If  $\Delta G_{\text{system}} = 0$ , the system has attained equilibrium.  
(C) If  $\Delta G_{\text{system}} = 0$ , the system is still moving in a particular direction.  
(D) If  $\Delta G_{\text{system}} < 0$ , the process is not spontaneous.
26. A process must be spontaneous (feasible) if  
(A) Entropy of system increases  
(B) Energy of system decreases  
(C) Gibbs free energy decreases  
(D) Entropy of universe increases
27. Heat liberated for an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K. What will be Gibb's free energy change for the process  
(A) 1200 cal (B)  $-1200 \text{ cal}$  (C) 400 cal (D)  $-400 \text{ cal}$
28. Which of the following extensive variable will increase during isothermal compression of an ideal gas-  
(A) U (B) S (C) H (D) G


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**$\Delta G$  for chemical reaction**

29. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?  
 (A) endothermic and decreasing disorder (B) exothermic and increasing disorder  
 (C) endothermic and increasing disorder (D) exothermic and decreasing disorder
30. For the reaction at  $25^\circ\text{C}$ ,  $\text{X}_2\text{O}_4 (\text{l}) \longrightarrow 2\text{XO}_2 (\text{g})$   
 $\Delta H = 2.1 \text{ Kcal}$  and  $\Delta S = 20 \text{ cal K}^{-1}$ . The reaction would be  
 (A) spontaneous (B) non-spontaneous (C) at equilibrium (D) unpredictable
31. For the reaction at  $298 \text{ K}$ ,  $2\text{A} + \text{B} \longrightarrow \text{C}$   
 $\Delta H = 100 \text{ kcal}$  and  $\Delta S = 0.050 \text{ kcal K}^{-1}$ . If  $\Delta H$  and  $\Delta S$  are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous?  
 (A)  $1000 \text{ K}$  (B)  $1500 \text{ K}$  (C)  $2000 \text{ K}$  (D)  $2500 \text{ K}$
32. For the reaction at  $300 \text{ K}$   
 $\text{A}(\text{g}) + \text{B}(\text{g}) \longrightarrow \text{C}(\text{g})$   
 $\Delta U = -3.0 \text{ kcal}$  ;  $\Delta S = -10.0 \text{ cal/K}$   
 value of  $\Delta G$  is?  
 (A)  $-600 \text{ cal}$  (B)  $-6600 \text{ cal}$  (C)  $-6000 \text{ cal}$  (D)  $-6 \text{ cal}$
33. What can be concluded about the values of  $\Delta H$  and  $\Delta S$  from this graph?




- (A)  $\Delta H > 0, \Delta S > 0$  (B)  $\Delta H > 0, \Delta S < 0$  (C)  $\Delta H < 0, \Delta S > 0$  (D)  $\Delta H < 0, \Delta S < 0$
34. What is the free energy change ( $\Delta G$ ) when  $1.0$  mole of water at  $100^\circ\text{C}$  and  $1 \text{ atm}$  pressure is converted into steam at  $100^\circ\text{C}$  and  $1 \text{ atm}$  pressure?  
 (A)  $80 \text{ cal}$  (B)  $540 \text{ cal}$  (C)  $620 \text{ cal}$  (D) zero
35. What is the free energy change ( $\Delta G$ ) when  $1.0$  mole of water at  $100^\circ\text{C}$  and  $1 \text{ atm}$  pressure is converted into steam at  $100^\circ\text{C}$  and  $2 \text{ atm}$  pressure?  
 (A) Zero cal (B)  $540 \text{ cal}$  (C)  $517.13 \text{ cal}$  (D)  $510 \text{ cal}$

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36.  $\Delta G$  for the conversion of 2 mol of  $C_6H_6(l)$  at  $80^\circ C$  (normal boiling point) to vapour at the same temperature and a pressure of 0.2 atm is  
 (A)  $-9.44 \text{ Kcal/mol}$  (B)  $-2.27 \text{ Kcal/mol}$   
 (C)  $-1.135 \text{ Kcal/mol}$  (D) zero
37.  $H_2O(s) \xrightarrow{2\text{atm}, 273.15K} H_2O(l)$   
 The correct set of sign of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  respectively for the above given process is :  
 (A) +, +, + (B) +, -, + (C) -, +, + (D) -, -, +
38. For hypothetical reversible reaction,  $\frac{1}{2} A_2(g) + \frac{3}{2} B_2(g) \longrightarrow AB_3(g)$ ;  $\Delta H = -20 \text{ KJ}$   
 if standard entropies of  $A_2$ ,  $B_2$  and  $AB_3$  are 60, 40 and  $50 \text{ JK}^{-1} \text{ mole}^{-1}$  respectively. The above reaction will be in equilibrium at the temperature :-  
 (A) 400 K (B) 500 K (C) 250 K (D) 200 K
39. Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and  $50 \text{ JK}^{-1} \text{ mol}^{-1}$ , respectively for the reaction,  
 $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$ ,  $\Delta H = -30 \text{ kJ}$  to be at equilibrium, the temperature will be :-  
 (A) 1250 K (B) 500 K (C) 750 K (D) 1000 K
40. Following reaction is in equilibrium at  $477^\circ C$ ,  $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g)$ ;  $\Delta H = -30 \text{ kJ}$ .  
 If standard entropy of  $N_2(g)$  and  $NH_3(g)$  are 60 and  $50 \text{ J mole}^{-1} \text{ K}^{-1}$  respectively then what is the standard entropy of  $H_2(g)$  at same temperature ?  
 (A)  $40 \text{ J mole}^{-1} \text{ K}^{-1}$  (B)  $60 \text{ J mole}^{-1} \text{ K}^{-1}$  (C)  $80 \text{ J mole}^{-1} \text{ K}^{-1}$  (D)  $120 \text{ J mole}^{-1} \text{ K}^{-1}$

### Variation of $\Delta G$ with temperature

41. At 298 K,  $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5737 \text{ KJ/mol}$  &  $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6333 \text{ KJ/mol}$ .  
 Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume  $\Delta_r C_p = 0$  for this temperature change  
 (A) 0 (B) 2 kJ/mol (C) 24 kJ/mol (D) 23.07 kJ/mol
42. For the hypothetical reaction,  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$   
 $\Delta_r G$  and  $\Delta_r S$  are  $20 \text{ kJ/mole}$  and  $-20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively at 200 K.  
 If  $\Delta_r C_p$  is  $20 \text{ JK}^{-1} \text{ mol}^{-1}$  then  $\Delta_r H$  at 400 K is :-  
 (A)  $20 \text{ kJ/mole}$  (B)  $7.98 \text{ kJ/mole}$  (C)  $28 \text{ kJ/mole}$  (D) None of these

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### $\Delta G$ and non PV work

43. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the "capturing" of energy from the reaction is done through electrical process (non- PV work) then calculate maximum available energy which can be captured by combustion of 3.42 gm of sucrose.

**Given :**  $\Delta H_{\text{combustion}} (\text{sucrose}) = -6000 \text{ kJ mol}^{-1}$

$\Delta S_{\text{combustion}} = 180 \text{ J/Kmol}$  & Body temperature is 300 K.

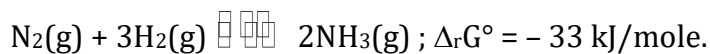
- (A) 60 kJ                      (B) 59.46 kJ                      (C) 0.54 kJ                      (D) 60.54 kJ

### Thermodynamic and equilibrium constant

44. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :-  
 (A)  $-\Delta G^\circ = RT \ln K$     (B)  $\Delta G = RT \ln K$     (C)  $-\Delta G = RT \ln K$     (D)  $\Delta G^\circ = RT \ln K$
45. The value of  $\Delta G^\circ$  for a reaction in aqueous phase having  $K_c = 1$ , would be:  
 (A)  $-RT$                       (B)  $-1$                       (C) 0                      (D)  $+RT$
46. If  $\Delta G^\circ > 0$  for a reaction then :  
 (A)  $K_P > 1$   
 (B)  $K_P < 1$   
 (C) The products predominate in the equilibrium mixture  
 (D)  $K_P = 1$
47. For the reaction takes place at certain temperature  $\text{NH}_4\text{HS(s)} \rightleftharpoons \text{NH}_3\text{(g)} + \text{H}_2\text{S(g)}$ , if equilibrium pressure is X bar, then  $\Delta_r G^\circ$  would be :-  
 (A)  $-2 RT \ln X$                       (B)  $-RT \ln (X - \ln 2)$   
 (C)  $-2 RT (\ln X - \ln 2)$                       (D) None of these
48. For a reaction  $\text{A(g)} \rightleftharpoons \text{B(g)}$  at equilibrium, the partial pressure of B is found to be one fourth of the partial pressure of A. The value of  $\Delta G^\circ$  of the reaction  $\text{A(g)} \rightleftharpoons \text{B(g)}$  is  
 (A)  $RT \ln 4$                       (B)  $-RT \ln 4$                       (C)  $RT \log 4$                       (D)  $-RT \log 4$

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49. What is  $\Delta_r G$  (KJ/mole) for synthesis of ammonia at 298 K at following sets of partial pressure :



[Take  $R = 8.3 \text{ J/K mole}$ ,  $\log 2 = 0.3$  ;  $\log 3 = 0.48$ ]

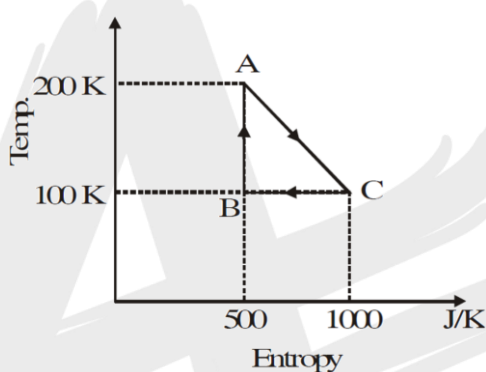
Gas	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
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Pressure (atm)	1	3	0.02
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(A) + 6.5	(B) - 6.5	(C) + 60.5	(D) - 60.5
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**TS diagram**

50. Efficiency of reversible cycle show will be



(A) 33.33%	(B) 56%	(C) 66.6%	(D) 16.7%
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