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CY101-Assignment I

1. A sample consisting of 1.00 mol Ar is expanded isothermally at 0^oC from 22.4 dm^3 to 44.8 dm^3 (a) reversibly (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU and ΔH.
(Ans. (a) $\Delta U = \Delta H = 0; q = 1.57KJ, w = -1.57KJ$, (b) $\Delta U = \Delta H = 0; q = 1.13KJ, w = -1.13KJ$, (c) $\Delta U = \Delta H = 0; q = 0, w = 0$.)

2. Consider a system consisting of 2.0 mol of a perfect gas, initially at 25^oC and 10 atmand confined to a cylinder of cross-section 10 cm^2. It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved through 20 cm. Assume $C_{V,m} = 28.8$ J K^{-1} mol^{-1}. Calculate q, w, ΔU, ΔT and ΔS.
(Ans. $q = 0, w = -20J, \Delta U = -20J, \Delta T = -0.347K, \Delta S = 0.60JK^{-1}$)

3. Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of N_2 gas of mass 14 gm at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible process (b) an isothermal irreversible expansion against $p_{ext} = 0$ and (c) an adiabatic reversible process.
(Ans. (a) $\Delta S_{gas} = 2.9JK^{-1}, \Delta S_{surr} = -2.9JK^{-1}, \Delta S_{total} = 0$, (b) $\Delta S_{gas} = 2.9JK^{-1}, \Delta S_{surr} = 0, \Delta S_{total} = 2.9JK^{-1}$, (c) $\Delta S_{gas} = 0, \Delta S_{surr} = 0, \Delta S_{total} = 0$)

4. The enthalpy of vaporization of chloroform is 29.4 KJ mol^{-1} at its normal boiling point of 334.88K. Calculate (a) the entropy of vaporization of chloroform at this temperature and (b) the entropy change of the surroundings, if the vapourization occurs reversibly.
(Ans. (a) $\Delta S_{vap} = 87.8JK^{-1}mol^{-1}$, (b) $\Delta S_{surr} = -87.8JK^{-1}mol^{-1}$)

5. Suppose S is a function of p and T. Show that $TdS = C_p dT - \alpha TV dp$, where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the expansion coefficient.(Hint: Use Maxwell relation for $\left(\frac{\partial S}{\partial p}\right)_T$.)

6. Suppose that 3.0 mol of N_2 occupies 36 cm^3 at 300K and expands to 60 cm^3. Calculate ΔG for the process.
(Ans. -3.8 J)

7. Naphthalene melts at 80.2^{o}C. If the vapor pressure of the liquid is 10 Torr at 85.8^oC and 40 Torr at 119.3^oC, use the Clausius-Clapeyron equation to calculate the enthalpy of vaporization, the normal boiling point and the entropy of vapourization at the boiling point.
(Ans. $\Delta H_{vap} = 48.5KJmol^{-1}, T_b = 489K, \Delta S_{vap} = 99JK^{-1}mol^{-1}$)

8. The temperature dependence of the vapour pressure of solid sulfur dioxide can be approximately represented by the relation $\log(p/Torr) = 10.5916 - 1871.2K/T$ and that of liquid SO_2 by $log(p/Torr) = 8.3186 - 1425.7K/T$. Estimate the temperature and pressure at the triple point of SO_2.
(Ans. $T_3 = 196.0K, p_3 = 11.1Torr$)

9. In the gas phase reaction $2A + B \rightleftharpoons 3C + 2D$, it was found that when 1.00 mol of A, 2.00 mol of B and 1.00 mol of D were mixed and allowed to come to equilibrium at 25^{o}C, the resulting mixture contained 0.90 mol of C at a total pressure of 1.00 bar. Calculate (a) K_p, (c) K, (b) ΔG^o.
(Ans. (a) $K_p = 0.33$, (b) $\Delta G^o = 2.8Jmol^{-1}$)

10. The molecules of a gas have two states of internal energy with statistical weights g_1, g_2 and energies 0, ϵ respectively. Calculate the contribution of these states to the specific heat of the gas.
(Ans. $C_V = \frac{N\epsilon^2 g_1 g_2 e^{\epsilon/kT}}{kT^2(g_1 e^{\epsilon/kT} + g_2)^2}$)

11. A system of particles occupying single-particle levels and obeying Maxwell Boltzmann statistics is in thermal contact with a heat reservoir at temperature T. If the population distribution in the non-degenerate energy levels is as shown, what is the temperature of the system?

$Energy(eV)$	$Population$
12.9×10^{-3}	25%
4.3×10^{-3}	75%

(Ans. $T = 91.59K$)

12. N particles are distributed among three states having energies $E = 0$, $E = kT$ and $E = 2kT$. If the total equilibrium energy of the system is $1000kT$, what is the value of N?
(Ans. $N \approx 2400$)

13. One mole of N_2 gas undergoes a change from an initial state described by T=200K, P=5 bar to a final state described by T=400K and 20 bar. Treat N_2 as the van der Walls gas with parameters a = 0.137 Pa m^6 mol^{-2} and b=3.87x10^{-5} m^3 mol^{-1} We use the path N_2(g, T=200K, P=5 bar) → N_2(g, T=200K, P=20 bar) → N_2(g, T=400K, P=20bar) keeping in mind that all paths will give the same answer for ΔU of the overall process. Compute ΔU.

(-132 J)

14. Using $\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial P}\right)_T + V$, show that μ_{JT} for an ideal gas is zero.

15. A substance exists in two solid modifications 'α' and 'β' as well as liquid and vapor. At a pressure of 1 atm, 'α' is stable at low temperatures than 'β', which melts at a still higher temperature to form the liquid. Also, 'α' is denser than the liquid but 'β' is less dense than the liquid. Assuming that no metastable equilibria are observed, sketch the pressure temperature phase diagram showing the significance of each point, line and region. Also indicate all the triple points in the diagram.

16. Water is vaporized reversibly at atmospheric pressure. The heat of vaporization is 40.69 kJ/mol. (a) what is the value of ΔS for the water? (b) what is the value of ΔS for the water plus the heat reservoir at 100 ^{0}C? (Ans.: a. 109.04 J/Kmol; b. 0 J/Kmol)

17. What is the entropy of mixing of 1 mol of oxygen with 1 mole of nitrogen at 25 0C, assuming that they are ideal gases? (Ans.: 11.526 J/K)

18. How many degrees of freedom are there for the following system;
$CuSO_4.5H_2O$ (s) in equilibrium with $CuSO_4$ (s) and H_2O (g)

(Ans.: 1)

19. Determine whether

$(i)\ \frac{dx}{y} - \frac{x}{y^2}dy$ *and* $(ii)\ xy^2dx - x^2ydy$ are exact differentials.

20. Calculate ΔS° for the reduction of Al_2O_3 by H_2 gas.

Standard entropies:

$S^0(Al_2O_3, s) = 51\ JK^{-1}mol^{-1}$

$S^0(H_2, g) = 131\ JK^{-1}mol^{-1}$

$S^0(H_2O, g) = 189\ JK^{-1}mol^{-1}$

$S^0(Al, s) = 28\ JK^{-1}mol^{-1}$

21. What is the entropy change for the freezing of 3.33 grams of an alcohol, C_2H_3OH, at 373.2 K given that ΔH = – 40.7 kJ/mol?