No. of printed pages : _04_

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SARDAR PATEL UNIVERSITY
M. Sc. (Semester – III) (CBCS) Examination
Monday, 4ᵗʰ January 2021
10:00 a.m. to 12:00 noon
PS03CPHC23 : Selected Topics in Physical Chemistry – I

Total Marks : 70

Note : Figures to the right indicate full marks.

(Useful constants are, $h = 6.63 \times 10^{-34}$ J.s, $R = 1.987$ cal.K^{-1} mol^{-1}, $k = 1.38 \times 10^{-23}$ J.K^{-1}, $k = 0.695$ cm^{-1}, $N = 6.023 \times 10^{23}$ mol^{-1})

Q. 1 (a) Select the correct answer from the alternatives given below to the each question;   (08)

[i] Permutation of the word "**COVID VACCINE**" is;

(a) 12 ! /(2! × 2! × 2!)   (b) 12 ! / (3! × 2! × 2!)

(c) (2! × 2! × 2!) / 12 !   (d) (3! × 2! × 2!) / 12 !

[ii] Arithmetic mode is;

(a) the observation having minimum frequency

(b) the observation having maximum frequency

(c) the observation having zero value

(d) equal to mean value

[iii] Which of the following distribution is an example of continuous distribution?

(a) Binomial   (b) Poisson

(c) Gaussian (normal)   (d) Mean

[iv] The value of zero point energy is _____ .

(a) $h\upsilon$ (b) 3/2 $h\upsilon$

(c) ½ $h\upsilon$ (d) 5/2 $h\upsilon$

[v] Electrode from which electron leave the cell is known as;

(a) anode   (b) cathode

(c) negative electrode   (d) counter electrode

[vi] Anodization of metal involves formation of _____ .

(a) a thin layer of metal oxide   (b) a thin layer of metal carbonate

(c) a thin layer of pure metal   (d) a thin layer of rust formation

[vii] The exchange current density is ; (where A is the area of electrode)

(a) $J_0 = i_0 . A$ (b) $J_0 = i_0 / A$

(c) $J_0 = i_0$ (d) $J_0 = A / i_0$

[viii] The Gerischer model is only applicable for;

(a) No interaction between electrode and the redox system

(b) No interaction between the redox system and electrode

(c) Strong interaction between the redox system and electrode

(d) Weak interaction between the redox system and electrode

[P. T. O.]

Q.1 (b) Do as directed. (16)

    (i) Match the following. (1 Marks × 5)

	Column I		Column II
(A)	Z_{trans}	**(a)**	$\pi_{nuclei}\,(2S_n + 1)$
(B)	Z_{rot}	**(b)**	$g_0\,e^{-\epsilon_0/kT}$
(C)	Z_{ele}	**(c)**	$\dfrac{8\pi^2 I\,C\,k\,T}{h}$
(D)	Z_{vib}	**(d)**	$\left(\dfrac{2\pi m k T}{h^2}\right)^{3/2}.V$
(E)	g_n	**(e)**	$\pi_{modes}\left(\dfrac{1}{1 - e^{-h\upsilon/kT}}\right)$

    (ii) For the following, fill in the blanks. (1 Marks × 5)

      (a) Combination, $_nC_r$ = _____.

      (b) According to Fermi-Dirac statistics, $N_j / (g_j - N_j)$ = _____.

      (c) In the equation, $S = k \ln W$, k is non other than _____.

      (d) The value of transfer coefficient, α is always between _____ and _____.

      (e) With increase in temperature, degree of dissociation for an electrolyte _____.

    (iii) Answer the following in TRUE/FALSE. (1 Marks × 6)

      (a) Gerischer model is applicable to semiconductor electrode.

      (b) A fuel cell is typically produce a voltage of 0.6 to 0.7 V.

      (c) Tafel equation is $\eta = a + b \log i$.

      (d) The DHO equation is $\wedge = \wedge_0 - (A - B\wedge_0)\,\sqrt{C}$.

      (e) Fermion possesses asymmetric wave-function.

      (f) In terms of partition function, $G = - NK \ln Z / N$.

Q.2 Answer the following in short; (ANY SEVEN) (14)

    [a] Derive the equation, $PV = NKT$.

    [b] Enlist properties of Binomial distribution.

    [c] The probability of breaking a test tube in single experiment is 0.1. Calculate the probability for not breaking a test tube in ten such experiment.

    [d] If two particles have to be distributed in three energy levels, enlist number of Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann distributed.

    [e] Write a note on Falkanhagen effect.

    [f] Discuss limitations of Arrhenius theory of electrolysis.

    [g] As per the Sterling approximation, what is value of $\ln N!$? Also define statistical weight.

    [h] Draw a figure representing electrical double layer.

    [i] State the equation that correlate current and the net rate of an electrode reaction.

Q.3 **[a]** For an assembly of a coin, derive the following relation; (04)

$$ln\ W/W_{max} = -2\ n^2/N$$

[b] The letters of the word "**PREPARE**" are placed in a box. One letter is taken from the (04) box at a time. If letters are taken out altogether, what is the probability that they spell out the word "**RARE**" in the correct order?

OR

Q.3 **[a]** Show that variance of Poisson distribution is **nP**. (04)

[b] A sulphuric acid plant makes acid with a mean concentration of 60 %. What is the (04) maximum value of the standard deviation to assure that 99 % or more of the acid has a concentration between 56 % and 64%?

Q.4 **[a]** Show that Entropy, S is independent of choice of energy zero. (04)

[b] According to Fermi Dirac statistics, show that **S = NK ln Z/N + U/T + NK**. (04)

OR

Q.4 **[a]** Write a note on Assembly partition function, **Z**. Discuss significance of **Z**. (04)

[b] The frequency of absorption band for CO associated with its vibrational transition is (04) 6.51×10^{13} per second. At what temperature does kT becomes equal to the energy of this vibrational transition?

**Q.5** **[a]** What is fuel cell ? Write down the reactions involved in it? (04)

[b] Enlist various applications of electrolysis. (04)

OR

Q.5 **[a]** Discuss the factors affecting the conductance of an electrolytic solution. (04)

[b] Calculate the weight of metallic chromium deposited from a solution of chromium (04) chloride ($CrCl_3$) by a current of 0.2 Ampere passing for 100 minutes. (At. Wt. of Cr = 52 g.mol^{-1})

Q.6 Consider the reaction; (08)

$$Na^+ + e^- \rightleftharpoons Na\ (Hg)$$
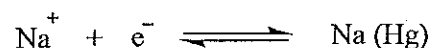
With the help of figures explain equilibrium and non-equilibrium conditions.

OR

Q.6 **[a]** Write a note on the standard rate constant, k. (04)

[b] According to Gerischer model, explain electron transfer mechanism between (04) semiconductor electrode and redox electrolyte.

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Proportion of the distribution lying to the right of $u = u_1$ i.e. $\dfrac{1}{\sqrt{2\pi}}\displaystyle\int_{u_1}^{\infty} e^{-u^2/2}\,du.$

u_1	0	1	2	3	4	5	6	7	8	9
0.0	.5000	.4960	.4920	.4880	.4840	.4801	.4761	.4721	.4681	.4641
0.1	.4602	.4562	.4522	.4483	.4443	.4404	.4364	.4325	.4286	.4247
0.2	.4207	.4168	.4129	.4090	.4052	.4013	.3974	.3936	.3897	.3859
0.3	.3821	.3783	.3745	.3707	.3669	.3632	.3594	.3557	.3520	.3483
0.4	.3446	.3409	.3372	.3336	.3300	.3264	.3228	.3192	.3156	.3121
0.5	.3085	.3050	.3015	.2981	.2946	.2912	.2877	.2843	.2810	.2776
0.6	.2743	.2709	.2676	.2643	.2611	.2578	.2546	.2514	.2483	.2451
0.7	.2420	.2389	.2358	.2327	.2296	.2266	.2236	.2206	.2177	.2148
0.8	.2119	.2090	.2061	.2033	.2005	.1977	.1949	.1922	.1894	.1867
0.9	.1841	.1814	.1788	.1762	.1736	.1711	.1685	.1660	.1635	.1611
1.0	.1587	.1562	.1539	.1515	.1492	.1469	.1446	.1423	.1401	.1379
1.1	.1357	.1335	.1314	.1292	.1271	.1251	.1230	.1210	.1190	.1170
1.2	.1151	.1131	.1112	.1093	.1075	.1056	.1038	.1020	.1003	.0985
1.3	.0968	.0951	.0934	.0918	.0901	.0885	.0869	.0853	.0838	.0823
1.4	.0808	.0793	.0778	.0764	.0749	.0735	.0721	.0708	.0694	.0681
1.5	.0668	.0655	.0643	.0630	.0618	.0606	.0594	.0582	.0571	.0559
1.6	.0548	.0537	.0526	.0516	.0505	.0495	.0485	.0475	.0465	.0455
1.7	.0446	.0436	.0427	.0418	.0409	.0401	.0392	.0384	.0375	.0367
1.8	.0359	.0351	.0344	.0336	.0329	.0322	.0314	.0307	.0301	.0294
1.9	.0287	.0281	.0274	.0268	.0262	.0256	.0250	.0244	.0239	.0233
2.0	.0228	.0222	.0217	.0212	.0207	.0202	.0197	.0192	.0188	.0183
2.1	.0179	.0174	.0170	.0166	.0162	.0158	.0154	.0150	.0146	.0143
2.2	.0139	.0136	.0132	.0129	.0125	.0122	.0119	.0116	.0113	.0110
2.3	.0107	.0104	.0102	.00990	.00964	.00939	.00914	.00889	.00866	.00842
2.4	.00820	.00798	.00776	.00755	.00734	.00714	.00695	.00676	.00657	.00639
2.5	.00621	.00604	.00587	.00570	.00554	.00539	.00523	.00508	.00494	.00480
2.6	.00466	.00453	.00440	.00427	.00415	.00402	.00391	.00379	.00368	.00357
2.7	.00347	.00336	.00326	.00317	.00307	.00298	.00289	.00280	.00272	.00264
2.8	.00256	.00248	.00240	.00233	.00226	.00219	.00212	.00205	.00199	.00193
2.9	.00187	.00181	.00175	.00169	.00164	.00159	.00154	.00149	.00144	.00139

[4]