

PHYSICAL CHEMISTRY - GRADUATE LEVEL PLACEMENT

DATA THAT MAY BE USEFUL FOR SOME QUESTIONS

Speed of light = $2.9979 \times 10^8 \text{ m sec}^{-1} = 2.9979 \times 10^{10} \text{ cm sec}^{-1}$

Universal Gas Constant = $8.3143 \text{ J K}^{-1} \text{ mol}^{-1} = 1.9872 \text{ cal K}^{-1} \text{ mol}^{-1}$
 $= 82.056 \text{ cm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

Faraday Constant = $96,487 \text{ coulomb equiv}^{-1}$

Avogadro Number = $6.0222 \times 10^{23} \text{ molecules (gram-mole)}^{-1}$

Boltzmann Constant = $1.3806 \times 10^{-23} \text{ J K}^{-1} = 1.3806 \times 10^{-16} \text{ erg K}^{-1}$

Planck's Constant = $6.626 \times 10^{-34} \text{ J sec} = 6.626 \times 10^{-27} \text{ erg sec}$

PART I - THERMODYNAMICS

1. The internal energy, E , of a system is a function of mass, volume, and temperature. The differential of E for a constant mass is

- (1) $dE = dV + dT$
- (2) $dE = Vdp - SdT$
- (3) $dE = (\partial E/\partial V)_T dV + (\partial E/\partial T)_V dT$
- (4) $dE = E(dV/dT) + E(\partial T/\partial V)$

2. According to the Laws of Thermodynamics, differentials of the following are exact:

- (1) work and enthalpy.
- (2) energy and work.
- (3) entropy and heat.
- (4) energy and entropy.

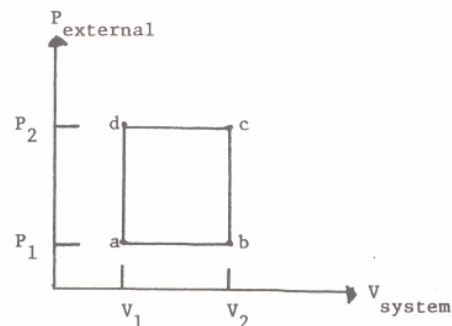
3. An "exact differential," df , as the term is ordinarily used in Thermodynamics, satisfies the condition

- (1) $\oint df = 0$
- (2) $\int_A^B df = f_A - f_B$
- (3) $\frac{\partial M}{\partial x} = \frac{\partial N}{\partial y}$ where $df = M(x,y)dx + N(x,y)dy$
- (4) that its line integral between two fixed points is dependent on the path.

4. When 0.5 mole of an ideal gas at 0°C is compressed isothermally from 1.00 atm to 2.00 atm

- (1) $\Delta G = 0$
- (2) no heat is absorbed by the gas.
- (3) the work done on the gas is +787 joules.
- (4) $\Delta E = 0$

5.



The following statements refer to changes between the thermodynamic states a,b,c,d of a system occurring by the paths shown on the $P_{\text{ext}}-V_{\text{ext}}$ diagram. Which statement is true?

- (1) For the process a**→**b**→**c**→**d**→**a the work done by the system is zero.
 - (2) For the process a**→**b**→**c**→**d**→**a the entropy change of the system is greater than zero.
 - (3) For the process a**→**b**→**c the work done by the system is $P_1(V_2-V_1)$.
 - (4) For the process a**→**d the work done by the system is $V_1(P_2-P_1)$.
6. At temperature sufficiently high for full contribution from vibrational motion, the molar heat capacity at constant pressure, C_p , of an ideal diatomic molecule is
- (1) $\frac{9}{2} R$
 - (2) $\frac{7}{2} R$
 - (3) $\frac{5}{2} R$
 - (4) $\frac{3}{2} R$
7. The equation $\left(\frac{\partial G}{\partial P}\right)_{X,m} = V$ is correct when the system is in internal equilibrium and $X =$
- (1) T
 - (2) S
 - (3) H
 - (4) V

1. The osmotic pressure of a solution is
- (1) the pressure of solvent vapor above a solution.
 - (2) the pressure that must be applied to the solution to increase the activity of the solvent in solution to equal that of the pure solvent.
 - (3) the pressure that must be applied to the pure solvent to increase its activity to equal that of the solvent in the solution.
 - (4) increased by increasing the mole fraction of solvent in the solution.

2. The entropy of a system (degeneracy = Ω) is

- (1) $kT \ln \Omega$
- (2) $-k \ln \Omega$
- (3) $k \ln \Omega$
- (4) $k/\ln \Omega$

3. A system of N_t molecules that is in thermal equilibrium has N_o molecules in a nondegenerate ground state of zero energy. Let

$$Q = \sum_i e^{-\epsilon_i/kT}$$

where the summation over i includes all allowed states of a molecule. The number N_a of molecules in the nondegenerate state of energy ϵ_a is given by

- (1) $N_t e^{-\epsilon_a/kT}$
- (2) $(N_t/Q) e^{-\epsilon_a/kT}$
- (3) $(1/Q) e^{-\epsilon_a/kT}$
- (4) $(N_o/Q) e^{-\epsilon_a/kT}$

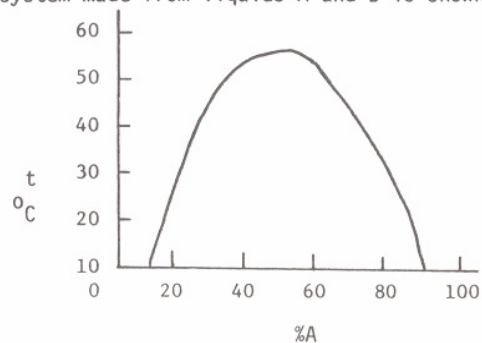
11. The partition function for a two-state system, state 0 and state 1, $\epsilon_0 = 0$, $\epsilon_1 > 0$, neither state degenerate, is

- (1) 0 at absolute zero.
- (2) $e^{-\epsilon_1/kT}$ at low temperatures.
- (3) $e^{-\epsilon_1/kT}$ at high temperatures.
- (4) 2 at very high temperatures.

12. For HCl the energy of the first excited vibrational state, relative to the ground state, is 5.73×10^{-20} J. At equilibrium at 25°C , the number of molecules in the first excited vibrational state relative to the number in the ground state is

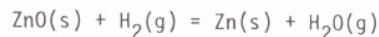
- (1) 2.3×10^{-23}
- (2) 8.9×10^{-7}
- (3) 6.6×10^{-2}
- (4) 7.2×10^{-2}

13. A phase diagram for two-component liquid system made from liquids A and B is shown below.



- (1) A system consisting of 70% A at 20°C will possess a phase which is rich in A but has a smaller A content as the temperature rises.
- (2) A system consisting of 80% A at 10°C will form a single phase.
- (3) A system consisting of 40% A at 60°C will form two phases.
- (4) Statements (1), (2), and (3) are all correct.

14. Consider the reaction:



	$\Delta H_f^\circ, 298$	$\Delta G_f^\circ, 298$
ZnO(s)	-348 kJ mole ⁻¹	-318 kJ mole ⁻¹
H ₂ O(g)	-242 kJ mole ⁻¹	-228 kJ mole ⁻¹

From these data, estimate the temperature at which the equilibrium constant for this reaction is approximately unity.

- (1) 700 K
- (2) 1300 K
- (3) 1900 K
- (4) 2500 K

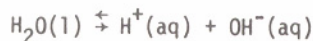
15. Two phases are said to be in mutual equilibrium (i.e., they can coexist indefinitely) when

- (1) they are at their critical temperature.
- (2) the mole fraction of each component, the temperature, and the pressure are each the same in the two phases.
- (3) the temperature, the pressure and the chemical potential of each component are the same in the two phases.
- (4) no molecules are being transferred from one phase to another.

16. The following thermochemical data are for 25°C.

	ΔH_f^0	C_p^0
$H_2O(l)$	-286 kJ mole ⁻¹	75.3 joule mole ⁻¹ K ⁻¹
$H^+(aq)$	0	0
$OH^-(aq)$	-230 kJ mole ⁻¹	-148 joule mole ⁻¹ K ⁻¹

For the self-ionization of water,



the value of ΔH^0 at 35°C is

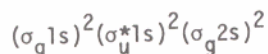
- (1) 58.1 kJ mole⁻¹ (3) 55.9 kJ mole⁻¹
 (2) 56.6 kJ mole⁻¹ (4) 53.8 kJ mole⁻¹
17. The "liquid junction potential" which arises in electrochemical cells having separate anode and cathode solutions is due to
- (1) polarization of electrodes.
 (2) temperature fluctuations in the cell.
 (3) measurement of the potential at zero current.
 (4) the difference in mobility of anions and cations.
18. Suppose $S = -p_1 \ln p_1 - p_2 \ln p_2$ with $p_1 + p_2 = 1$. Which statement follows?
- (1) S vanishes for $p_2 = p_1$
 (2) S vanishes for $p_2 = -p_1$
 (3) dS/dp_2 vanishes for $p_2 = p_1$
 (4) None of the above.
19. The heat of vaporization of water at 100°C is 40.6 kJ mole⁻¹. If one mole of liquid water is reversibly vaporized at 100°C and 1 atm, which of the following statements is incorrect?
- (1) $q = 40.6$ kJ (3) $\Delta G = 3.1$ kJ
 (2) $\Delta E = 37.5$ kJ (4) $\Delta S = 109$ J K⁻¹
20. A certain gas has a heat capacity at constant pressure of $C_p = 3.5 R$ cal mol⁻¹ K⁻¹ at 298 K and does not absorb any radiation in the infrared or microwave regions. The most likely identity of the gas is
- (1) Ar (2) CO (3) N₂ (4) H₂O

PART II - QUANTUM CHEMISTRY

21. If λ is wavelength of light, ν is the frequency of light, c is the speed of light, h is Planck's constant and $\bar{\nu} = 1/\lambda$, the energy of the photon is given by
- (1) $h\lambda$ (2) $hc\bar{\nu}$ (3) h/ν (4) $\frac{h}{\lambda}$
22. In the hydrogen atom the energy (wavenumber) of the transition 3s → 2s is 15,240 cm⁻¹. The energy (wavenumber) of the transition 2s → 1s is close to
- (1) 82,300 cm⁻¹ (3) 22,860 cm⁻¹
 (2) 30,480 cm⁻¹ (4) 7,620 cm⁻¹
23. The ionization energy of the H-atom is 13.6 eV. The ionization energy of the Li⁺⁺ ion is
- (1) 122.4 eV (3) 1.5 eV
 (2) 40.8 eV (4) 4.5 eV
24. Suppose ψ_m and ψ_n are normalized eigenfunctions of a particular hermitian operator and the subscripts m and n refer to non-degenerate eigenstates. The integral over all space, $\int \psi_m \psi_n d\tau$, is equal to
- (1) zero if $m = n$ (3) one if $m \neq n$
 (2) zero if $m \neq n$ (4) the total energy of the system.
25. Which function is not an eigenfunction of the operator $\frac{\partial^2}{\partial x^2}$?
- (1) e^{ikx} (3) e^{-kx^2}
 (2) $\cos kx$ (4) $\sin kx$
26. Quantum states described by the wavefunctions ψ_a , ψ_b and ψ_c are all associated with an energy level E_1 . This
- (1) violates the condition that proper wavefunctions must be unique.
 (2) is an example of three-fold degeneracy.
 (3) can only occur when the Hamiltonian operator contains cross terms.
 (4) is an example of a complete set of wavefunctions.

27. Which of the following ψ -functions is definitely NOT antisymmetric in its two arguments?
- (1) $\psi(x_1, x_2) = -\psi(x_2, x_1)$
- (2) $\psi(x_1, x_2) = g(x_1)h(x_2) - g(x_2)h(x_1)$
- (3) $\psi(x_1, x_2) = \begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) \\ \phi_1(x_2) & \phi_2(x_2) \end{vmatrix}$
- (4) $\psi(1, 1) = 1$
28. The determinant $\begin{vmatrix} 2 & -3i \\ 6i & 7 \end{vmatrix}$ has the value
- (1) -4 (3) 23
- (2) (14 + 18i) (4) 32
29. A one dimensional box of length L is formed by having infinite potential barriers at the walls and zero potential within the box. For a particle of mass m placed in this box, quantum mechanics predicts that the separation between successive allowed energy levels will increase with
- (1) increasing L.
- (2) decreasing m.
- (3) decreasing principal quantum number.
- (4) none of the above.
30. The electric dipole moment of the diatomic molecule $N^{14}N^{15}$ is very nearly
- (1) 13 Debye. (3) 0.13 Debye.
- (2) 1.3 Debye. (4) 0 Debye.
31. The orbital designations s, p, d, f, etc. to describe an electron in the hydrogen atom are most closely related to
- (1) the spin angular momentum of the electron.
- (2) the kinetic energy of the electron.
- (3) the angular momentum of the electron about the nucleus.
- (4) the component of the electron angular momentum in the direction of an applied field.
32. The electronic configuration of an excited state of the C^+ ion is
- (1) $(1s)^2(2s)^2(2p)^2$ (3) $(1s)^2(2s)^2(3s)^1$
- (2) $(1s)^2(2s)^1(2p)^3$ (4) $(1s)^2(2s)^2(2p)^1$
33. The period for one vibration of the N_2 molecule is approximately
- (1) 10^{-14} second (3) 10^{-11} second
- (2) 10^{-12} second (4) 10^{-9} second
34. The fundamental vibration frequency of the A-B molecule, expressed in wavenumbers, is $N \text{ cm}^{-1}$. The difference in energy between the third vibrational state and the lowest vibrational state is
- (1) $\frac{7hcN}{2}$ (3) $\frac{5}{2}hcN$
- (2) $2hcN$ (4) N
35. Pure rotational absorption spectra can be
- (1) observed for any diatomic molecule.
- (2) observed usually in the ultraviolet region of the spectrum.
- (3) used to calculate precise values for interatomic distances.
- (4) used to calculate precise values for the force constants of chemical bonds
36. A so-called " π orbital" in a diatomic molecule is characterized by
- (1) a nodal plane between the nuclei and perpendicular to the bond axis.
- (2) two nodal planes parallel to the bond axis, one above and one below it.
- (3) an absence of nodes, except possibly in the radial coordinate.
- (4) a nodal plane containing the bond axis
37. A low-resolution infra-red spectrum of $H^{35}Cl$ shows a band centered at 2886 cm^{-1} . If $H^{35}Cl$ is replaced by $D^{35}Cl$ the center of the band will be observed at
- (1) 2069 cm^{-1} (3) 4026 cm^{-1}
- (2) 2886 cm^{-1} (4) 2550 cm^{-1}

38. Which of the statements below is true concerning a diatomic molecule with a ground state molecular orbital configuration of



- (1) The molecule is necessarily heteronuclear.
- (2) The molecule has a total electronic spin quantum number $S = 1$.
- (3) The molecule has a total electronic orbital angular momentum quantum number $\Lambda = 1$.
- (4) The molecule has what is usually called a single bond between the atoms.
39. For most organic molecules an electronic transition from the ground state to the first excited singlet state is an allowed process, but a transition to the lowest triplet state is forbidden. Which statement is true?
- (1) This is an example of the operation of a selection rule based on the conservation of spin angular momentum.
- (2) This implies that fluorescence will be an intrinsically slow process.
- (3) This implies that phosphorescence will be an intrinsically fast process.
- (4) None of the above.
40. Sodium crystallizes in a body-centered cubic lattice in which the edge of a unit cube is b . X-ray diffraction indicates that the distance between adjacent 110 planes in the lattice is

- (1) b (2) $\sqrt{2} b$ (3) $\frac{\sqrt{2}}{2} b$ (4) $\frac{\sqrt{3}}{3} b$

 PART III - DYNAMICS

41. At 100 K, the average speed of a helium atom is $7.27 \times 10^2 \text{ m sec}^{-1}$. At 400 K, the average speed of a helium atom is
- (1) $7.27 \times 10^2 \text{ m sec}^{-1}$
- (2) $14.54 \times 10^2 \text{ m sec}^{-1}$
- (3) $29.08 \times 10^2 \text{ m sec}^{-1}$
- (4) $52.9 \times 10^6 \text{ m sec}^{-1}$

42. According to the Maxwellian distribution of molecular speed, u , i.e.

$$P(u)du = Au^2 e^{-\frac{mu^2}{2kT}} du$$

where A is a constant, the most probable speed is

- (1) $\sqrt{\frac{3kT}{M}}$ (3) $\sqrt{\frac{8kT}{m}}$
- (2) $\sqrt{\frac{2kT}{m}}$ (4) $\frac{3}{2} kT$
43. The average speed of a collection of gas molecules with a Maxwellian distribution (see question 42) is given by

- (1) the solution of the equation, $\frac{dP(u)}{du} = 0$

(2) $A \int_0^{\infty} u e^{-\frac{mu^2}{2kT}} du$

(3) $A \int_0^{\infty} u^2 e^{-\frac{mu^2}{2kT}} du$

(4) $A \int_0^{\infty} u^3 e^{-\frac{mu^2}{2kT}} du$

44. If a and n are constants, the derivative $\frac{d}{dx}(\ln ax^n)$ is equal to

(1) nax^{n-1} (3) $\frac{na}{x}$

(2) $\frac{1}{(nax^{n-1})}$ (4) $\frac{n}{x}$

45. The rate law for the reaction $A \rightarrow B$ is

$$-\frac{d[A]}{dt} = k[A]^2$$

After 10 minutes $[A] = (1/2) [A]_0$, where $[A]$

is the initial concentration of A . After 20 minutes $[A]$ is

(1) $(1/4) [A]_0$

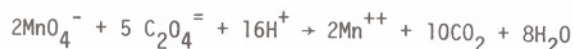
(2) $(1/8) [A]_0$

(3) $(1/3) [A]_0$

(4) indeterminate.

46. The three transport processes, diffusion, viscosity, and thermal conductivity are driven respectively, by gradients in
- (1) concentration, momentum, and temperature.
 - (2) concentration, density, and temperature.
 - (3) temperature, concentration, and density.
 - (4) momentum, density, and temperature.

47. Consider the overall chemical reaction



Which of the following statements concerning the reaction rate is necessarily true?

- (1) $\frac{d[\text{Mn}^{2+}]}{dt} = k[\text{MnO}_4^-]^2$ where k is a constant.
 - (2) $\frac{d[\text{CO}_2]}{dt} = Ae^{-E/RT}$ where A is a constant.
 - (3) $-\frac{d[\text{C}_2\text{O}_4^{2-}]}{dt} = \frac{5}{2} \frac{d[\text{Mn}^{2+}]}{dt}$
 - (4) $-\frac{d[\text{MnO}_4^-]}{dt} = 5 \frac{d[\text{CO}_2]}{dt}$
48. A first-order reaction
- (1) is always unimolecular.
 - (2) has a half-life that is dependent on concentration.
 - (3) has the rate law $dc/dt = -kc$, where c represents concentration and k is greater than zero and is independent of c .
 - (4) does not actually occur in nature.

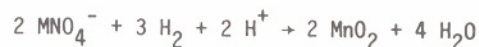
49. The initial rate of the gas reaction



is independent of the partial pressure of NO. This observation indicates that

- (1) the NO molecule is involved in the rate-determining step.
- (2) the NO is involved in an equilibrium prior to the rate-determining step.
- (3) the NO reacts subsequently with a species produced in the rate-determining step.
- (4) the experimenter must have made a mistake in his measurement because the rate must depend upon the pressure of NO.

50. For the reaction



these data hold:

Exp. No.	$[\text{MnO}_4^-]$	$[\text{H}_2]$	$[\text{H}^+]$	$-\left(\frac{d[\text{H}_2]}{dt}\right)_{\text{init}}$
1	0.005	0.0005	0.001	R_0
2	0.001	0.0005	0.001	$0.2 R_0$
3	0.001	0.0015	0.001	$0.6 R_0$
4	0.005	0.0005	0.010	R_0

Which rate law is consistent with these data?

- (1) $-\frac{d[\text{H}_2]}{dt} = k[\text{MnO}_4^-]^2 [\text{H}_2]^3 [\text{H}^+]^2$
 - (2) $-\frac{d[\text{H}_2]}{dt} = k[\text{MnO}_4^-] [\text{H}_2]$
 - (3) $-\frac{d[\text{H}_2]}{dt} = k[\text{MnO}_4^-] [\text{H}_2] [\text{H}^+]$
 - (4) $-\frac{d[\text{H}_2]}{dt} = k[\text{MnO}_4^-]^2 [\text{H}_2]^3$
51. According to the Maxwellian distribution of speeds of a collection of molecules, the fraction of molecules with speeds between u and $u + du$ is

$$P(u)du = Au^2 e^{-\frac{mu^2}{2kT}} du$$

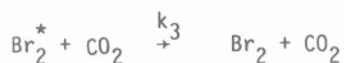
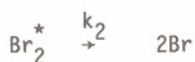
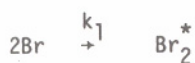
where A is a constant. The Maxwellian distribution of kinetic energies, $p(E)dE$, is

- (1) $\left(\frac{A}{2}\right) \left(\frac{2}{m}\right)^{3/2} E^{1/2} e^{-E/kT} dE$
- (2) $A \left(\frac{2}{m}\right) E e^{-E/kT} dE$
- (3) $AE^2 e^{-E/kT} dE$
- (4) $\left(\frac{A}{2}\right) \left(\frac{2}{m}\right)^{3/2} E^2 e^{-E/kT} dE$

52. Doubling the chain length, or molecular weight of a linear random-coil polymer has the effect of increasing both its root-mean-square end-to-end distance and its radius of gyration by a factor of

- (1) 1 (2) 1.4 (3) 2.0 (4) 4.0

53. A mechanism for the recombination of gaseous bromine atoms in the presence of carbon dioxide is



When the excited bromine molecules, Br_2^* , are at a steady-state concentration, the rate law for Br_2 formation is predicted to be

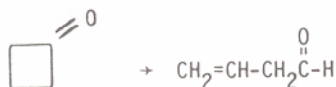
(1) $k_3[\text{Br}]^2[\text{CO}_2]$

(2) $\frac{k_1 k_3}{k_2} [\text{Br}]^2 [\text{CO}_2]$

(3) $\frac{k_1 k_3 [\text{Br}]^2 [\text{CO}_2]}{k_2 + k_3 [\text{CO}_2]}$

(4) $\frac{k_1 k_2}{k_3} [\text{CO}_2]$

54. A ring opening reaction such as



- (1) should increase in rate with the application of pressure.
 (2) should be scarcely dependent on reaction temperature.
 (3) should be markedly accelerated by substituting ^{18}O for ^{16}O .
 (4) should have a large positive entropy of activation.

55. An assumption by which the highly useful "Transition-State Theory" of chemical reactions is usually derived is that

- (1) equilibrium exists between reactants and products.
 (2) equilibrium exists between reactants and an activated complex.
 (3) the atoms in the reactant molecules move at constant velocity and in straight lines.

(4) all reactions have negligible activation energy.

56. In a certain gaseous reaction at 227°C the fraction of collisions that result in reaction is 4×10^{-10} . The activation energy, of the reaction, (in joules/mole) is close to

(1) 9×10^4 (3) 5×10^3

(2) 8×10^6 (4) -5×10^3

57. Diffusion generally plays a rate-determining role in

- (1) slow reactions in liquid solution.
 (2) fast reactions in liquid solution.
 (3) gas-phase reactions with high activation energies.
 (4) unimolecular reactions in the gas phase.

58. For a second-order rate constant, the Arrhenius equation,

$$k = Ae^{-E/RT}$$

may be interpreted in terms of Absolute Reaction Rate Theory. For such a case a small experimental value for the frequency factor A indicates that

- (1) the activation energy is unusually large.
 (2) the entropy of activation is highly positive.
 (3) the entropy of activation is zero.
 (4) the entropy of activation is highly negative.

59. The diffusion coefficient of a particular t-RNA molecule in solution is $D = 10^{-11} \text{ m}^2/\text{sec}$. What is the time required for such molecules produced at one point in the nucleus of a cell to diffuse to a root-mean-square displacement of 10^{-6} m , corresponding to the diameter of the whole cell?

(1) 0.002 sec (3) 1 sec

(2) 0.05 sec (4) 10 sec

60. A series of rate experiments on a model reaction $A \rightarrow B + C$ were carried out with three different initial concentrations of A. It was found that the time required for 50% of A to react was inversely proportional to the initial concentration. A reasonable conclusion is that the reaction is

(1) zero order in A (3) second order in A

(2) first order in A (4) third order in A