(60%) Part 1. Only one answer is correct for each following question. 3 points will be given for a correct answer, 3 points will be deducted for an incorrect answer and no point for no answer.

( ) 1. What is the quantum mechanical operator for the classical energy E?
(1) $-\dfrac{i}{\hbar}\dfrac{\partial}{\partial t}$ (2) $\dfrac{i}{\hbar}\dfrac{\partial}{\partial t}$ (3) $\dfrac{\hbar}{i}\dfrac{\partial}{\partial t}$ (4) $-\dfrac{\hbar}{i}\dfrac{\partial}{\partial t}$

( ) 2. If you like to perform semiempirical molecular orbital calculations, which of the following packages should you use? (1) MOPAC (2) GAUSSIAN 90 (3) AMBER (4) MOLSCRIPT

( ) 3. Which of the following operators is not Hermitian? (1) d/dx (2) id/dx (3) d^2/dx^2

( ) 4. For a harmonic oscillator, what is the relation between the force constant k and the angular frequency ω? (1) $k \propto \omega^2$ (2) $k \propto \omega$ (3) $k \propto \sqrt{\omega}$ (4) $k \propto 1/\sqrt{\omega}$

( ) 5. What is the magnitude of the dipole moment of H_2O? (1) 0.58 D (2) 1.85 D (3) 2.58 D (4) 3.85 D.

( ) 6. How many normal modes of vibration are there for CO_2? (1) 3 (2) 4 (3) 5 (4) 6

( ) 7. Choose the molecule that will exhibit a pure rotational microwave spectrum (1) NF_3 (2) SF_6 (3) CH_4 (4) CO_2.

( ) 8. What is the degeneracy of a rotational level J for a spherical top

molecules (1) $2J+1$ (2) $(2J+1)^2$ (3) $2J(2J+1)$ (4) $(2J+1)(2J-1)$

( ) 9. What is the relationship between pK_a and the corresponding free energy ΔG? (1) $\Delta G \propto \log(pK_a)$ (2) $\Delta G \propto pK_a$ (3) $\Delta G \propto \exp(pK_a)$.

( ) 10. According to Transition State Theory, the rate constant is written as $A\exp(-\Delta G^* / k_B T)$, where ΔG^* is the activation free energy, k_B the Boltzmann constant and T temperature - what is the frequency factor A?
(1) $k_B T / \hbar$ (2) $k_B T / h$ (3) $\hbar / k_B T$ (4) $h / k_B T$.

( ) 11. Why is the rate constant in transition state theory the upper bound to the true rate constant? (1) It emphasizes too much on the transition state (2) It assumes that the reactant molecules is in accordance with the Maxwell-Boltzmann distribution (3) It neglects the recrossings of the reactant molecules (4) It is a very old theory.

( ) 12. In the molecule CO, which atom carries the negative partial charge?
(1) C (2) O (3) Both atoms carry zero partial charges.

( ) 13. The Morse potential is $V(r) = D[1 - \exp(-\alpha(r - r_e))]^2$. What is its harmonic force constant? (1) $D\alpha^2$ (2) $2D^2\alpha$ (3) $2D\alpha^2$ (4) $\sqrt{D}\alpha$

( ) 14. If l_x, l_y and l_z are the three components of the angular momentum operator l, then (1) $[l_x, l_y] = 0$ (2) $[l_y, l_x] = i\hbar l_z$ (3) $[l_y, l_z] = i\hbar l_x$

( ) 15. If G is the Gibbs free energy and A is the Helmholtz free energy, then what is $A - G$ (1) TS (2) $-H$ (3) PV (4) $-PV$ (T: temperature, S: entropy, H: enthalpy, P: pressure, V: volume).

( ) 16. $\left(\dfrac{\partial A}{\partial T}\right)_V =$? (1) S (2) $\left(\dfrac{\partial G}{\partial T}\right)_P$ (3) $\left(\dfrac{\partial E}{\partial T}\right)_V$ (4) $\left(\dfrac{\partial H}{\partial T}\right)_P$

( ) 17. For a wave function $\psi(x) = \left(\dfrac{a}{\pi}\right)^{1/4} \exp(-ax^2/2)$, what is the value of $<x>$? (1) $\sqrt{a}$ (2) $\dfrac{1}{2}\sqrt{a}$ (3) $\sqrt{a/2}$ (4) 0.

( ) 18. What is the ground state term for the atom: O? (1) $^3P_2$ (2) $^2P_{3/2}$ (3) $^4F_{3/2}$

( ) 19. What is the point group for C_2H_6 (in the skew conformation)? (1) D_{3d} (2) D_{3h} (3) D_{3d} (4) D_{2h}

( ) 20. What is the point group for cyclopropane (ignore hydrogens)? (1) D_{3d} (2) D_{3h} (3) D_{3d} (4) D_{2h}

Part 2. (40%) Answer the following questions and show your calculation.

(15) 1. Standard thermodynamic values at 25°C and 1 atm pressure.

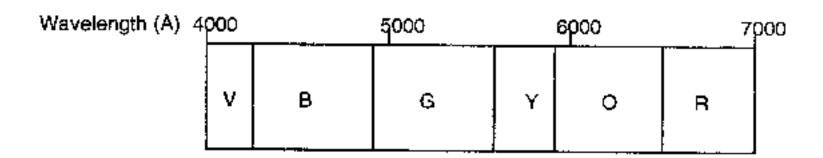| compounds	ΔG_f (kJ mol^{-1})
L-Alanine	
CH_3CHNH_2COOH(s)	-371.71
Benzene, C_6H_6(g)	129.66
Methane, CH_4(g)	-50.72
H_2O (aq)	-134.03
NH_3(g)	-16.45
NH_3(aq)	-26.50
C (s, graphite)	0
C (s, diamond)	2.90
H_2 (g)	0
NO (g)	86.55
NO_2 (g)	51.31
O_2 (g)	0
O_3 (g)	163.2

Use data from the table to answer the following questions.

(a) Is the reaction $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ spontaneous at 25°C

and 1 atm?

(b) A salesman wants to sell you a catalyst that allows benzene to be formed by passing $H_2(g)$ over carbon (graphite) at 25°C and 1 atm. Should you buy? Why?

(c) Is the reaction to form solid alanine, CH_3CHNH_2COOH, and liquid H_2O from $CH_4(g)$, $NH_3(g)$ and $O_2(g)$ spontaneous at 25°C and 1 atm?

(13) 2. Use the figure to decide what color flame would indicate the presence of barium in a sample of unknown composition. Barium atoms can undergo an electronic transition of energy 3.62×10^{-12} erg if a barium-containing material is heated on a Bunsen flame.

Wavelength (A) 4000   5000   6000   7000

| V | B | G | Y | O | R |

V-Violet B-Blue G-Green Y-Yellow O-Orange R-Red

(12) 3. The rate of a first order reaction increases from $r = 1.5 \times 10^{-2}$ sec^{-1} to $r_c = 4.6$ sec^{-1} at 260°C when a catalyst is added to the reaction. Calculate the decrease in the activation enthalpy H, assuming S°, the activation entropy, is not affected by the catalyst.