可使用計算機

Gas constant R= 8.31 J/K mol, Boltzmann constant k=1.38x10^{-23} J/K, Planck's constant h=6.62 x10^{-34} J s

I. (20 points/2 points each) Select the one choice that best completes the statement or answer that question.

1. Thermodynamics does NOT:
    A). describe the flow and interchange of heat, energy, and matter.
    B). allow the determination of whether a reaction is spontaneous.
    C). provide information on the rate of a reaction.
    D). consider heat flow and entropy production.
    E). consider the effect of concentration on net free energy change of a reaction.

2. Living systems are:
    A). closed systems exchanging only energy with the surroundings.
    B). isolated systems that are totally contained.
    C). open systems exchanging only energy with the surroundings.
    D). open systems exchanging both energy and matter with their surroundings.
    E). none of the above.

3. Enthalpy change, ΔH, is:
    A). the sum of heat absorbed and work.
    B). not a thermodynamic state function.
    C). a measure of disorder in a system.
    D). determined by pressure change at a constant temperature.
    E). equal to the heat transferred at constant pressure and volume.

4. Calorimetry measures _____ by a biochemical process.
    A). heat absorbed or given off   , ΔH,
    B). pressure change inside calorimeter created
    C). water pressure created
    D). entropy change, ΔS,
    E). volume change, ΔV, created

5. All are true for the Second Law of Thermodynamics EXCEPT:
    A) Systems tend to proceed from ordered states to disordered states.
    B) The entropy of the system plus surroundings is unchanged by reversible processes
    C) The entropy of the system plus surroundings increases for irreversible processes.
    D) All naturally occurring processes proceed toward equilibrium.
    E) None, all are true.

6. Entropy change, ΔS, is
    A). the sum of heat absorbed and work.
    B). not a thermodynamic state function.
    C). a measure of disorder in a system.
    D). determined by pressure change at a constant temperature.
    E) equal to the heat transferred at constant pressure and volume.

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7. Which example has the greatest increase in entropy, ΔS?

        A). freezing water

        B). sublimation of CO_2

        C). melting ice

        D). shattering glass

        E). boiling gasoline

8. Which equation <u>defines</u> a system at equilibrium?

        A). $\Delta G > 0$

        B). $\Delta G° = \Delta G$

        C). $\Delta G = 0$

        D). $\Delta G° = 0$

        E). $\Delta G = RT \ln ([products]/[reactants])$

9. Thermodynamic parameters (entropy, enthalpy, free energy, and internal energy) are given for an unknown enzyme. Explain which results would be expected for the breaking of hydrogen bonds and the exposure of hydrophobic groups from the interior during the unfolding process of a protein.

        A). Entropy change, ΔS, is zero

        B). Enthalpy change, ΔH, is positive

        C). The reaction is spontaneous

        D). Enthalpy change, ΔH, is negative

        E). Entropy change, ΔS, is positive

10. To predict whether pairs of coupled reactions will proceed spontaneously:

        A). Subtract the smaller from the larger ΔG.

        B). Sum the $\Delta G°$'s for each reaction.

        C). Add the ΔS values for each reaction at constant temperature.

        D). The absolute value of the positive $\Delta G°'$ must be larger than the value of the negative $\Delta G°'$.

        E) None are true.

II.

1. (10 points)

An enzymatic hydrolysis of fructose-1-P   (Fructose-1-P + H_2O $\rightleftharpoons$ Fructose + Pi)

was allowed to proceed to equilibrium at 25°C.   The original concentration of fructose-1-P was 0.2 M, but when the system had reached equilibrium the concentration of fructose 1-P was only 6.52 x 10^{-5} M. Calculate the equilibrium constant for this reaction and the standard free energy of hydrolysis of fructose 1-P.

2. (10 points)

Hexokinase catalyzes the phosphorylation of glucose from ATP, yielding glucose-6-P and ADP.   Please calculate the standard-state free energy change and equilibrium constant for the hexokinase reaction.($\Delta G°'$= -13.9 kJ/mol for glucose-6-P hydrolysis; $\Delta G°'$ = - 30.5 kJ/mol. for ATP hydrolysis to ADP)

3. (10 points)

The equilibrium constant for some process A $\rightleftharpoons$ B is 0.5 at 20°C and 10 at 30°C.   Assuming that $\Delta H°$ is independent of temperature, calculate $\Delta H°$ for this reaction.   Determine $\Delta G°$ and $\Delta S°$ at 20° and at 30°C.

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III.

1. The substance A can decompose in parallel into the substances B and C in first-order reactions:
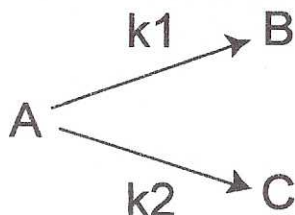

   (a) What's the integrated rate expression for the concentration of B and C as a function of time? Assuming the initial concentration [A]=a_0, [B]=0 and [C]=0. (b) What's the ratio of [B] to [C] at t=10 sec? (c) What's the ratio of [B] to [C] at t=100 sec? (7 points)

2. Consider the exchange reaction,

   $CH_3S^*H + C_2H_5SH$ <---> $CH_3SH + C_2H_5S^*H$
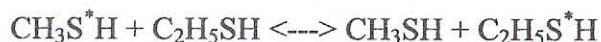
   where S* is a radioactive isotope present in tracer amounts, initially all in the CH_3SH molecules. What is the reaction order of the rate of exchange of S* between the two molecular species, CH_3S^*H and $C_2H_5S^*H$? Explain why. (5 points)

3. Many reactions catalyzed by enzymes frequently follow a law of the form υ = V [S] / (Km + [S]). At what condition, the order of the reaction will be (a) first order (b) zero order? where V and Km are constants, and [S] is the concentration of the substrate. (5 points)

4. What would be the units for the rate constant of a 3/2-order reaction? Use concentrations in mol/dm^3, time in second. (5 points)

5. A molecule that absorb light (I_a) may reemit the light in a process called fluorescence or phosphorescence (depending on the time scale), or lose its energy by collision with another molecule (Q); this is called quenching of fluorescence. Show that the intensity of fluorescence (I_f) is related to the intensity of the light absorbed (I_a) by the Stern-Volmer equation: $\frac{1}{I_f} = \frac{1}{I_a}(1 + \frac{k_q[Q]}{k_f})$ (7 points)
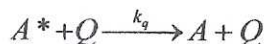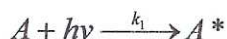
$$A + h\nu \xrightarrow{k_1} A^*$$
$$A^* + Q \xrightarrow{k_q} A + Q$$
$$A^* \xrightarrow{k_f} A + h\nu'$$

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6. What is the major factor that limits the maximum rate constant of a bimolecular reaction in gases? and in solutions? Explain. (5 points)

7. Explain the following terms: (1) elementary reaction (2) chain reaction (3) activation energy (4) catalyst (5) enzyme (5 points)

8. The compound CH3-O-N-O undergoes a cis-trans isomerization by internal rotation about the O-N bond. The half-life of the first-order conversion of the cis form was measured by NMR techniques as 10^{-6} s at 298 K. Assuming the entropy of the activation, $\Delta S^{\dagger}$=0, calculate the height of the barrier to rotation. How good an assumption do you think $\Delta S^{\dagger}$=0 would be? Explain. (6 points)

9. The chemical relaxation time for $H^+ + OH^- \longleftrightarrow H_2O$, with pH=7.0 is 36 μs. Calculate the rate constant. (5 points)