科目：物理化學(2004)　　校系所組：中大化學學系　清大化學系　交大應用化學系甲組

參考用

Give only one correct answer (單選題，每題五分，答錯倒扣一分):

1. A system had 150 kJ of work done on it and its internal energy increased by 60 kJ. How much energy did the system gain or lose as heat?
   A) The system gained 60 kJ of energy as heat.
   B) The system gained 90 kJ of energy as heat.
   C) The system gained 210 kJ of energy as heat.
   D) The system lost 90 kJ of energy as heat.
   E) The system lost 210 kJ of energy as heat.

2. If 2 mol of an ideal gas at 300 K and 3 atm expands from 6 L to 18 L and a final pressure of 1.2 atm in two steps: (i) the gas is cooled at constant volume until its pressure has fallen to 1.2 atm, and (ii) it is heated and allowed to expand against a constant pressure of 1.2 atm until its volume reaches 18 L, which of the following is correct?
   A) $w = 0$ for (i) and $w = -1.46$ kJ for (ii).
   B) $w = -4.57$ kJ for the overall process.
   C) $w = -6.03$ kJ for the overall process.
   D) $w = -4.57$ kJ for (i) and $w = -1.46$ kJ for (ii).
   E) $w = 0$ for the overall process.

3. Choose one statement to *correctly* elucidate the physical meanings of the *second law* of thermodynamics.
   A) It is impossible to construct a perpetual machine performing work in a cyclic process without affecting the surroundings.
   B) From any arbitrary state of any system there are a finite number of states arbitrarily close to the initial state that cannot be reached by an adiabatic process.
   C) Clausius stated that no process is possible in which the only transfer of energy is as heat transferred from a hotter to a colder system.
   D) In Kelvin-Planck statement, it states that heat obtained from the hot reservoir cannot transfer completely into work, therefore we can conclude that work cannot transfer completely into heat as well.
   E) The entropy change in any non-spontaneous process is positive. In other words, the process will continue until the entropy has increased to the maximum.

4. In the first half of the 19th century, Joule tried to measure the temperature change when a gas is expanded into a vacuum. However, the experimental setup was not sensitive enough so that Joule found no temperature change within the limit of his error. Soon afterward, Joule and Thomson devised a much more sensitive method to measure the temperature change upon expansion, known as Joule-Thomson effect. Regarding Joule's and Joule-Thomson's experiments, which one of the following equations is *incorrect*?

A) $\mu_J = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$

B) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

C) $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$

D) $\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P - V$

E) $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

5. Octane (C_8H_{18}) can be used to construct a fuel cell based on the oxidation of the compound with the energy (enthalpy) released by the following reaction:

$$C_8H_{18(l)} + \frac{25}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(l)} \quad \Delta H^0 = -5471\ \text{kJ}\cdot\text{mol}^{-1};\ \Delta G^0 = -5296\ \text{kJ}\cdot\text{mol}^{-1}.$$

A) The maximum work, including expansion and non-expansion types available through the combustion of the hydrocarbon at the standard state, is $-5296\ \text{kJ}\cdot\text{mol}^{-1}$.

B) The minimum heat that must be released into the surroundings at the standard state is $-175\ \text{kJ}\cdot\text{mol}^{-1}$.

C) The Helmholtz free energy change of combustion of the hydrocarbon at the standard state is $-5460\ \text{kJ}\cdot\text{mol}^{-1}$.

D) The internal energy change of combustion of the hydrocarbon at the standard state is $-5285\ \text{kJ}\cdot\text{mol}^{-1}$.

E) Consider a heat engine with $T_H = 600$ K and $T_C = 300$ K. The engine is running with the combustion of octane as a heat source. The ratio for the maximum work available from the heat engine to that available in an ideal electrochemical fuel cell using octane as a fuel is less than 0.5.

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6. For a real gas, we introduce the compression factor z by $z = \frac{V_m}{V_m^{ideal}} = \frac{PV_m}{RT}$ to reflect the extent of deviation from an ideal gas. There are many empirical equations being used to describe the behavior of a real gas, for examples, the van der Waals equation is given by $P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$, the virial equation can be expressed as

$$z = \frac{PV_m}{RT} = 1 + B(\frac{1}{V_m}) + C(\frac{1}{V_m})^2 + \ldots \quad \text{or} \quad z = \frac{PV_m}{RT} = 1 + B'P + C'P^2 + \ldots$$

A) The relationship between B and B' and between C and C' is the following: $B = B'RT$, $C = B'RT + C'R^2T^2$.

B) The expressions of virial coefficients B and C in terms of the van der Waals parameters a and b are $B = b - \frac{2a}{RT}$, $C = b^2$.

C) This Boyle temperature T_B in terms of the van der Waals parameters can be expressed as $T_B = \frac{2a}{Rb}$.

D) The slope of z as a function of P as $P \to 0$ in terms of the van der Waals parameters can be determined as $\lim_{P\to 0}\left(\frac{\partial z}{\partial P}\right)_T = B' = \frac{B}{RT} = \frac{1}{RT}\left(b - \frac{2a}{RT}\right)$.

E) For a van der Waals gas, the slope of z versus P curve as $P \to 0$ has a maximum value at the temperature $T_{max} = \frac{2a}{bR}$.

7. The densities of a given solid and liquid of molecular weight 122.5 at its normal melting temperature of 427.15 K are 1075 and 1012 kg m^{-3}, respectively. If the pressure is increased from 1 bar to 120 bar, the melting temperature increases to 429.35 K.

A) The molar entropy change of the fusion process is $34.8\ \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

B) The molar entropy change of the fusion process is $38.4\ \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

C) The enthalpy change of fusion at 1 bar and 427.15 K is $16.4\ \text{kJ}\cdot\text{mol}^{-1}$.

D) The enthalpy change of fusion at 1 bar and 427.15 K is $14.6\ \text{kJ}\cdot\text{mol}^{-1}$.

E) The volume of the system does not change upon fusion.

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8. The phase equilibrium between water and its vapor is $H_2O(l) \rightleftharpoons H_2O(g)$. The vapor pressure of a small droplet (is not the same as the vapor pressure of its bulk phase. At the standard state (T and P°), the vapor pressure of bulk water is P_0.

A) The Gibbs energy change of vaporization of bulk water at the standard state can be expressed as $\Delta G^\circ_{vap} = RT\,ln\frac{P_0}{P^\circ}$.

B) The vapor pressure of bulk water under an external pressure of P_x atm of inert gas at the standard state can be expressed as $P = P^\circ \exp(\frac{V_m^l P_x}{RT})$, where V_m^l represents the molar volume of the liquid phase.

C) The vapor pressure of water droplets with radius = r can be expressed as $\ln\left(\frac{P}{P^\circ}\right) = \frac{2\gamma V_m^l}{rRT}$, where γ represents the surface tension of the water droplets.

D) When the phase equilibrium is reached at the liquid-vapor interface at constant T, we have the following valid expressions: $(\mathrm{d}A^{liq})_T = -(\mathrm{d}A^{vapor})_T$, $\mu^{liq} = \mu^{vapor}$.

E) None of the above statements is correct.

9. In an ideal binary solution, the mole fractions of the two components satisfy $x_1 + x_2 = 1$ and the vapor pressures of the two components obey Raoult's law. Assuming that the vapor pressures of components 1 and 2 are P_1^* and P_2^*, respectively.

A) The total vapor pressure (P_{tot}) can be expressed as $P_{tot} = P_1^* + x_2(P_1^* - P_2^*)$.

B) If the mole fractions of components 1 and 2 in the gas phase are y_1 and y_2, respectively, P_{tot} can be expressed as $P_{tot} = \frac{P_1^* P_2^*}{P_2^* + y_2(P_2^* - P_1^*)}$.

C) An ideal solution is made from 5 mol of benzene ($P_1^* = 96.4$ Torr at 298 K) and 3.25 mol of toluene ($P_2^* = 28.9$ Torr at 298 K) at 298 K and 1 bar pressure, then $\Delta G_{mix} = 8.25 \times 8.314 \times 298 \times (\ln 0.606 + \ln 0.394)$.

D) At 298 K, if the pressure of the benzene-toluene mixture above-mentioned is reduced from 1 bar, the first vapor appears at $P_{tot} = 125.3$ Torr.

E) None of the above statements is correct.

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10. Many solutions consist of nonvolatile solutes that have limited solubility in a volatile solvent. Colligative properties such as boiling point elevation, freezing point depression, and osmotic pressure are found to depend only on the solute concentration and not on the nature of the solute.
   - A) Define the osmotic coefficient as $\phi = -(n_1/n_2)\ln a_1$ (where 1 and 2 represent solvent and solute, respectively; a_1 is the activity of the solvent), the freezing point depression can be expressed as $\Delta T_f = T_f^* - T_f = \phi K_f m$, where $K_f = M_1 R (T_f^*)^2 / 1000 \Delta H_{fus}$ and m is the concentration of solute in molality.
   - B) The freezing point depression is usually larger than the boiling-point elevation because the boiling point is larger than the melting point.
   - C) The osmotic pressure (Π) can be expressed as $\Pi = RT \ln a_1 / \bar{V}_1 \approx \phi cRT$, where c is the solute concentration in molarity, $\bar{V}_1$ is the molar volume of the solvent.
   - D) Purification of sea water is based on the concept of reverse osmosis. If Π = 23 atm for sea water, the work to be done to obtain one mol of pure water from sea water can be estimated to be $\Pi \bar{V}_1 = 23 \times 0.018 = 0.414\ \mathrm{kJ \cdot mol^{-1}}$.
   - E) None of the above statements is correct.

11. An excited state molecule M* can emit fluorescence, $M^* \rightarrow M + h\nu$, with the fluorescence rate constant $k_1 = 2\times10^{6}$ sec^{-1}. Molecule Q can quench the fluorescence through the reaction of $M^* + Q \rightarrow M + Q$ with $k_2 = 1\times10^{-11}$ cm^3 molecule^{-1} sec^{-1}. After excitation with a pulsed laser, M* is produced at t_0. What is the lifetime of the measured fluorescence decay at [Q]= 3×10^{17} molecule cm^{-3} ?
   - A) 2.0×10^{-7} sec
   - B) 5.0×10^{-7} sec
   - C) 2.0×10^{-6} sec
   - D) 2.5×10^{-6} sec
   - E) 5×10^{-6} sec

12. The vibrational frequency of $H^{35}Cl$ is 2990 cm^{-1}. What is the zero point energies of $D^{35}Cl$?
   - A) 438 cm^{-1}
   - B) 876 cm^{-1}
   - C) 1057 cm^{-1}
   - D) 1495 cm^{-1}
   - E) 2114 cm^{-1}

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13. If the masses of proton and neutron become twice of their present values (while the electron mass is still the present value), which of the following is correct for a usual hydrocarbon molecule?

A) The UV/Visible absorption spectra will shift to the red by more than 10%.
B) The IR absorption spectra will shift to the red by more than 10%.
C) Both UV/Visible absorption spectra and IR absorption spectra will shift to the red by more than 10%.
D) Light of short wavelength (by more than 10%) is needed in the photo-ionization experiment.
E) Light of longer wavelength (by more than 10%) can do the job of photo-ionization.

14. The root mean square speed of nitrogen molecules in air at 420 K is 707 m/s in a certain container. If the gas is allowed to expand to more than twice its original volume, the root mean square velocity of nitrogen molecules drops to 500 m/s. What is the temperature after the gas has expanded?

A) 297 K.
B) 210 K.
C) 420 K.
D) 105 K.
E) 250 K.

15. A possible mechanism for the reaction $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ is given below.

$2NO_{(g)} \xrightarrow{k1} N_2O_{2(g)}$ k_1, slow
$N_2O_{2(g)} \xrightarrow{k-1} 2NO_{(g)}$ k_{-1}, fast
$N_2O_{2(g)} + O_{2(g)} \xrightarrow{k2} 2NO_{2(g)}$, k_2, slow

Application of the steady-state approximation gives

A) $[N_2O_2] = 0$.
B) $k_1[NO]^2 - k_2[N_2O_2][O_2] = 0$.
C) $[N_2O_2] = (k_1/k_2)[NO]^2$.
D) $k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[N_2O_2][O_2] = 0$.
E) $[N_2O_2] = (k_1/k_{-1})[NO]^2$.

16. For X + $CH_4 \rightarrow HX + CH_3$ reaction: Given that the activation energy is 9.2 kJ/mol and the pre-exponential factor is 2.2×10^{12} cm^3 mol^{-1} sec^{-1} (1 cm^{-1} = 12 J/mol; R= 8 J mol^{-1} K^{-1}; N_A= 6×10^{23} molecules/mol; *ln* 10 = 2.3). What is the rate constant at 500 K?

A) 2.2×10^{12} cm^3 mol^{-1} sec^{-1}.
B) 9.6×10^{11} cm^3 mol^{-1} sec^{-1}.
C) 2.2×10^{11} cm^3 mol^{-1} sec^{-1}.
D) 2.2×10^{10} cm^3 mol^{-1} sec^{-1}.
E) 2.2×10^{13} cm^3 mol^{-1} sec^{-1}.

17. The electronic symmetry of the ground-state OH radical is $^2\Pi$. How many electrons are distributed in the π orbitals?

A) 0.
B) 1.
C) 2.
D) 3.
E) 4.

18. Which of the following describes best the Franck-Condon principle?

A) Nuclei are much heavier than electron, such that nuclei move much slower.
B) The vibrational wave function can be approximated as the model of Harmonic Oscillator.
C) The vibrational wave functions of different vibrational states are normalized and orthogonal to each other.
D) During an electronic transition, a change from one vibrational energy level to another will be more likely to happen if the two vibrational wave functions overlap more significantly.
E) The electronic wave function can be solved by fixing the positions of nuclei.

19. Due to nuclear spin statistics, para-H_2 has only even rotational quantum states. The energy gap between N=0 and N=2 rotational states is 360 cm^{-1}. What is the rotational constant of H_2.
    - A) 180 cm^{-1}.
    - B) 120 cm^{-1}.
    - C) 90 cm^{-1}.
    - D) 72 cm^{-1}.
    - E) 60 cm^{-1}.

20. A transition state of a chemical reaction must have the feature of
    - A) having one negative vibrational frequency.
    - B) being a maximum on any potential energy curve.
    - C) being a maximum on the potential energy surface.
    - D) being a minimum on the potential energy surface.
    - E) zero potential energy gradient.