Physical Chemistry (II) Examination Paper

2. Statistical Mechanics of Independent Particle Systems

I Choice (1 point for each, totally 30 points)

1. For the ideal liquid mixture, it is____________

   A：independent non-localized-particle system；

   B：dependent localized-particle system；

   C：independent localized-particle system.

2. The particles such as atoms, molecules, and ions in a crystal is____________.

   A：independent non-localized-particle system；

   B：dependent localized-particle system；

   C：localized-particle system.

3. Which of the following is an independent non-localized-particle system ______?

   A：a crystal at 0 K；　B：ideal liquid mixture；　C：ideal gas mixture

4. The lowest energy level of the translational kinetic energy is ____________

   A：$\varepsilon_{\mathrm{t}}=\dfrac{3h^2}{mV^{2/3}}$；　B：0；　C：$\varepsilon_{\mathrm{t}}=\dfrac{3h^2}{8mV^{2/3}}$

5. For a translational level, its energy is $\varepsilon_{\mathrm{t}}=\dfrac{7h^2}{4mV^{2/3}}$, the degeneracy of the level $g_{\mathrm{t},i}$ is __________________

   A：6；　B：5；　C：4

6. The ratio of the degree of the degeneracy of NO molecules at the first excited vibration level to its ground state is __________________

   A：1；　B：2；　C：3

7. The vibrational energy of CO molecule in the k^{th} energy level is higher than that in $k\text{-}1^{\mathrm{th}}$ energy level by__________________

   A：0.2 $h\nu$；　B：0.5 $h\nu$；　C：$h\nu$

8. Among different energy levels, which one is related to system volume________?

   A.vibrational energy level；B. rotational energy level；C.translational energy level

9. Among different energy levels, which one has the equal energy level space____?

   A.vibrational energy level；B. rotational energy level；C.translational energy level

10. For N_2 at room temperature, which of the following has the largest energy level space______________?

A.vibrational energy level; B. rotational energy level; C.translational energy level

11. At the same volume, the large the mass of particles, __________the translational energy level space.

A：unchanged; B：the larger; C：the smaller

12. The larger the volume,_________the translational energy level space.

A：unchanged; B：the larger; C：the smaller

13. The larger the rotational moment of inertia,_________the rotational energy level space.

A：unchanged; B：the larger; C：the smaller

14. The larger the vibrational frequency,_________the vibrational energy level space.

A：unchanged; B：the larger; C：the smaller

15. 7 distinguishable particles are distributed in 3 energy levels with the degeneracy of 1, 3, 2; the energy of ε_0, ε_1, ε_2, and the particle distribution of 3, 3, 1, the number of the microscopic states is_________.

A：6560; B：7560; C：8560

16. For a system composed of a large number of particles，when ω_{max}/Ω is small，$\ln\omega_{max}/\ln\Omega$ is closed to ___________.

A: 0; B: 1; C: 2

17. At normal temperature, the ratio of the number of particles distributed on any excited states N_v and that on the ground state N_0, N_v/N_0 is ______.

A: <1; B: =1; C: >1

18. At normal temperature, the ratio of the number of particles distributed on any excited states N_v and that on the neighboring state N_{v-1}, N_v/N_{v-1} is ________.

A: <1; B: =1; C: >1

19. For diatomic molecules at room temperature, with the increase of the energy level J, the number of particles distributed in the J level, N_J_______________.

A：decreases; B：increases;

C：increases first , then decreases, with a maximum value.

20. For a system composed of N particles distributed in two energy levels, the energy are $\varepsilon_1=0$, $\varepsilon_2=\varepsilon$, and the degeneracy are g_1 and g_2, then, the molecular partition function q is_____________________.

A: $g_1 + g_2\exp(-\varepsilon/kT)$; B: $g_1 + g_2\exp(\varepsilon/kT)$; C: $g_1g_2\exp(-\varepsilon/kT)$

21. When $T\rightarrow\infty$, the ratio of N_2 molecules distributed in the rotational energy levels of J=1 and J=0, N_1/N_0 =__________________

A: 2; B: 3; C: 4

22. It is known that the ground level are non-degenerate. At 400 K, for a diatomic molecular AB, $q_0 = 1.02$, the ratio of the number of particles distributed on the ground level N_0 and the total number of particles N is ____________.

A: 0.98; B: 1; C: 1.02

23. Among the following conclusions, the correct one is______.

A: $\left(\frac{\partial q_\mathrm{t}}{\partial V}\right)_T \neq 0$; B: $\left(\frac{\partial q_\mathrm{r}}{\partial V}\right)_T \neq 0$; C: $\left(\frac{\partial q_\mathrm{v}}{\partial V}\right)_T \neq 0$

24. At the same temperature and volume, which of the following gas has approximately the same translational partition function as N_2 ____________.

A: CO; B: H_2; C: NO

25. The mass ratio of A and B is M_A/M_B = 4, at the sanme temperature and volume, the ratio of the translational partition function q_{tA}/q_{tB} is____________________.

A: 4; B: 8; C: 12

26. At 298.15k and 101.325Pa, __________ has the largest molar translational entropy.

A: H_2; B: CH_4 C: CO_2

27. The rotational temperature Θ_r of N_2 and CO are 2.89K and 2.78K, respectively. The ratio of the rotational partition function $q_{\mathrm{r,N_2}}/q_{\mathrm{r,CO}}$ =_________________.

A: 0.381; B: 0.481; C: 0.581___

28. At 298.15k and 101.325Pa, the molar translational entropy of __________ is approximately equal to N_2

A: CO; B: CH_4 C: CO_2

29. For a non-localized-particle system, the total number of microscopic states is $\Omega = \mathrm{e}^L$, the entropy S of the system is___________.

A: 0.5R B: R C: 1.5R

30. The mass and the moment of inertia of the diatomic molecule CO are approximately equal to those of diatomic molecule N_2, At 25°C, $S^\ominus_{\mathrm{m,N_2}}$ ______ $S^\ominus_{\mathrm{m,CO}}$.

Suppose the vibration has little contributions to the entropy,

A: > B: = C: <

II (5 points for each, totally 10 points)

1. A system is composed of large amount of particles freely in three-dimensional translational movement. The relation among volumes V, particle mass m and temperature T is $h^2/(8mV^{2/3}) = 0.100\ kT$. Calculate the ratio of the particle number distributed in the energy level of $14h^2/(8mV^{2/3})$ and $3h^2/(8mV^{2/3})$.

2. X molecules are distributed in two energy levels with $\varepsilon_1 = 6.1\times10^{-21}$ J, $\varepsilon_2 = 8.4\times10^{-21}$J, the corresponding degeneracy are $g_1 = 3$, $g_2 = 5$. Suppose it is an independent-particle system, calculate the ratio of the particle number between these two levels when the temperature is 300K and 3000K, respectively.

III (10 points)

Given that, the molar mass of H_2 is M=2.0g.mol^{-1}, the rotational temperature $\Theta_r = 85.4\text{K}$, the vibrational temperature $\Theta_v = 6100\text{K}$, when the temperature is 298.15K, calculate:

1. The molecule translational partition function of H_2 in a cube of 1 m^3.
2. The molecule rotational partition function of H_2.
3. The molecule vibrational partition function of H_2, q_{0v}.
4. The ratio of the particle number between the first excited vibrational level and vibrational ground level.

IV (10 points)

1. Suppose a molecular vibrational energy level spacing is $\Delta\varepsilon_V = 5.942\times10^{-20}\,\text{J}$. At 298 K, what is the ratio of number of molecule between two neighboring energy levels?
2. Suppose vibrational energy level spacing is $\Delta\varepsilon_V = 0.43\times10^{-20}\,\text{J}$. At 298 K, what is the ratio of number of molecule between two neighboring energy levels?.
3. What can you conclude from the comparison of the above two calculation results?

V (10 points)

For a independent non-localized-particle system, the relation between entropy and molecular function is $S = Nk\ln(q/N) + U/T + Nk$. Prove that

$$A = -NkT\ln(q/N) - NkT\ ,\quad G = -NkT\ln(q/N) - NkT + NkT(\partial\ln q/\partial\ln V)_{T,N}\ .$$

VI (10 points)

Given that the relation between the entropy and the molecular partition function of a independent non-localized-particle system is $S = Nk\ln(q/N) + U/T + Nk$.

1. Prove that the entropy of ideal monoatomic gas molecules is given by

$$S = \frac{5}{2}Nk + Nk\ln\left[\left(2\pi mkT\right)^{3/2} Vh^{-3}N^{-1}\right].$$

2. Calculate the molar entropy of Ar at its normal boiling point. Given that the normal boiling point of Ar is 87.3 K and its molar mass is 39.95 $\mathrm{g \cdot mol^{-1}}$.

VII (10 points)

For a localized-particle system with N particles, it is given that $\ln \Omega = N\ln q + U/kT$. Prove that $H = NkT\left[\left(\partial \ln q/\partial \ln T\right)_V + \left(\partial \ln q/\partial \ln V\right)_T\right]$, $U = NkT^2\left(\partial \ln q/\partial T\right)_V$ and $G = -NkT\left[\ln q - \left(\partial \ln q/\partial \ln V\right)_T\right]$.

VIII (10 points)

For 1 mol ideal monoatomic molecular gas, try to prove by statistical mechanics that when the temperature changes from T_1 to T_2, the entropy change at constant pressure is as 5/3 times large as that at constant temperature.