第七章　统计热力学练习题 答案

一、选择题)

1. [答]　(D)

2.　[答]　(B)

3.　[答]　(D)

4. [答]　(C)

5.　[答]　(B)

6.　[答]　(A)

7.　[答]　(B)

8. [答]　(A)

从 6 个可别粒子中拿出 3 个来编为一组，放在 N_0能级，再从 (6 - 3) 个可别粒子中拿出 2 个来编为一组，放在 N_1能级上，最后从 (6 - 3 - 2)个可别粒子中拿出 1，放在 N_2能级上。

此种分布的微态数为：

$$C_6^3 C_3^2 C_1^1 = \{6!/[3!(6-3)!]\} \times \{3!/[2!(3-2)!]\} \times \{1!/[1!(1-1)!]\} = 6!/(3!2!1!)$$

9.　[答]　(C)

10.　[答]　B

$$\frac{N_1}{N_0} = \frac{g_{e,1}\exp(-\varepsilon_1/kT)}{g_{e,0}\exp(-\varepsilon_0/kT)} = \frac{g_{e,1}}{g_{e,0}}\exp(-\Delta\varepsilon/kT) \qquad =0.184$$

11.　[答]　(D)

12. [答]　(A)

13. [答]　(C)

14.　[答]　(B)

15.　[答]　(D)

$F_r = G_r = -NkT\ln q_r$

$U_V = H_V = NkT \times [x/(e^x-1)]$

$C_{V,V} = C_{p,V} = Nk \times [x^2 e^x/(e^x-1)^2]$　　$x = \Theta_v/T$

$C_{p,t} = (5/2)Nk$　　$C_{V,t} = (3/2)Nk$

所以 $C_{p,t} \neq C_{V,t}$

16.　[答]　(D)

17.　[答]　(B)

18.　[答]　(C)

$$\Theta_v = hc\tilde{\nu}/k = 308.5\ \text{K}$$

19.　[答]　(B)

$$\Theta_t = h^2/(8\pi^2 Ik) = 2.78\ \text{K}$$

20. [答]　A　　因对 CO, $\sigma = 1$

对N_2, $\sigma = 2$

21. [答] (D)

22. [答] (D)

$C_{p,\mathrm{m}}/C_{V,\mathrm{m}}=(C_{p,\mathrm{t}}+C_{p,\mathrm{r}})/(C_{V,\mathrm{t}}+C_{V,\mathrm{r}})$

$=[(5/2)Nk+(3/2)Nk]/[(3/2)Nk+(3/2)Nk]$

$=1.33$

23. [答] (A)

$S_{\mathrm{r,m}}=R[\ln T/\sigma\Theta_{\mathrm{r}}+1]$

$\sigma(\mathrm{CO})=1$； $\sigma(N_2)=2$ 则$S_{\mathrm{m}}(\mathrm{CO})>S_{\mathrm{m}}(\mathrm{N_2})$

24. [答] (B)

$\varepsilon_{\mathrm{t}}=(h^2/8mV^{3/2})(n_x^2+n_y^2+n_z^2)$

$g_{\mathrm{t}}=3!/2!=3$ （设 $n_x=2$, $n_y=1$, $n_z=1$）

25. [答] (B)

26.

[答] (D)

二、填空题

27. [答] 1202 K

对第一振动激发态

$$\varepsilon_{\mathrm{v}}=(1+\frac{1}{2})h\nu=kT$$

$$T=\frac{3}{2}\Theta_{\mathrm{v}}=1202\ \mathrm{K}$$

28. [答] $\Delta S=S_2-S_1=k\ln(\Omega_2/\Omega_1)$

$$\Omega_2/\Omega_1=\exp(\Delta S/k)=\exp(3.03\times10^{23})$$

29. [答] $\varepsilon_{\mathrm{r}}=J(J+1)h^2/(8\pi^2I)=kT$

$$J(J+1)=8\pi^2IkT/h^2$$

$=107.2$

$J=10$

30. [答] $T=0.70$ K

$$\varepsilon_{\mathrm{r}}=J(J+1)h^2/(8\pi^2I)$$

第一激发态 $\varepsilon_{\mathrm{r}}=1\times(1+1)\times(h^2/8\pi^2T)=kT$

$$T=2h^2/(8\pi^2kr^2m/2)=0.70\ \mathrm{K}$$

31. [答] $T=0.691$ K

$$\varepsilon_{\mathrm{r}}=J(J+1)h^2/(8\pi^2I)=J(J+1)h^2/\left(8\pi\mu r^2\right)$$

$$\mu=m^2/(2m)=m/2=2.943\times10^{-20}\ \mathrm{kg}$$

当 J=0 时，$\varepsilon_1 - \varepsilon_0 = \Delta\varepsilon_r = kT = 2h^2/\left(8\pi\mu r^2\right)$

$T = 2h^2/\left(8\pi^2\mu r^2 k\right) = 0.691\,\mathrm{K}$

32. [答] $N_0 = (L/q)\times g_0\exp(-\varepsilon_0/kT) = L/q$
$= (6.023\times10^{23}\,\mathrm{mol^{-1}})/1.6 = 3.76\times10^{23}\,\mathrm{mol^{-1}}$

33. [答] $N_{i+1}/N_i = \exp(-\Delta\varepsilon/kT) = 0.352$

34. [答] $N_i = (N/q)\times g_i\exp(-\varepsilon_i/kT)$
近独立粒子体系，且为处于热力学平衡态的孤立体系

35. [答] $N_1/N_2 = g_1\exp(-\varepsilon_1/kT)/g_2\exp(-\varepsilon_2/kT)$

$=0.595$

36. [答] $N_{\nu=1}/N_{\nu=0} = 1.3\times10^{-5}$

$N_{\nu=1}/N_{\nu=0} = \exp(-h\nu/kT)$

$=1.3\times10^{-5}$

37. [答] 1000 K

$N_{\nu=2}/N_{\nu=0} = \exp(-2h\nu/kT) = [\exp(-h\nu/kT)]^2$

$=0.5414$

$\exp(-h\nu/kT) = (0.5414)^{\frac{1}{2}} = 0.7358$

$T = -h\nu/(k\ln0.7358) = 1000\ \mathrm{K}$

38. [答] $q = \sum\exp(-\varepsilon_i/kT)$

$=1+\exp(-\varepsilon/kT)+\exp(-2\varepsilon/kT)+\exp(-3\varepsilon/kT)+\cdots$
$=1+x+x^2+x^3+\cdots$
$=1/(1-x)=1/[1-\exp(-\varepsilon/kT)]$
$N_0/N = 1/q = 1-\exp(-\varepsilon/kT)$

$=1-\exp[-3.2\times10^{-20}/(1.38\times10^{-23}\times300)]$

$=0.9996$

39. [答] $N_1/N_0 = g_1\exp(-\varepsilon_1/kT)/g_0$

40. [答] $q = \sum_i g_i\exp(-\varepsilon_i/kT)$
处于热力学平衡态近独立粒子体系中的单个分子

41. [答] $A = -kT\ln q^N$
$A = -kT\ln q^N/N!$
$A = -kT\ln Z$

42. [答] f_t-$T^{1/2}$
f_r-$T^{1/2}$ f_v-T

43. [答] 乘积； $q_t.q_v.q_r.q_e.q_n$

44. [答] 0.368； 1.104

$N_2^*/N_1^* = \exp[-(U_2-U_1)/kT] = e^{-1} = 0.368$

$N_2^*/N_1^* = (g_2/g_1)\exp[-(U_2-U_1)/kT] = 1.104$

45. [答] $q = \sum_i g_i \exp(-\varepsilon_i / kT) = g_1 + g_2 \exp(-\varepsilon / kT)$

46. [答] $q_{t,2d} = (2\pi mkT/h^2) \times A$

47. [答] $q = g_1 \exp(-\varepsilon_1 / kT) + g_2 \exp(-\varepsilon_2 / kT) + g_3 \exp(-\varepsilon_3 / kT)$

=1+3exp(-100/200)+5exp(-300/200)=3.9353

48. [答] $\dfrac{q_r(^{18}O_2)}{q_r(^{16}O_2)} = \dfrac{m_{18}}{m_{16}}$

49.[答] $q_v = [1-\exp(-\Theta_v/T)]^{-1} = 1.556$

$f_v = q_v = 1.556$

50. [答] $q_v = 1/[1-\exp(-h\nu/kT)]$

$T \to 0$ 时, $q_v = 1$

51. [答] $\Theta_E = h\nu_E/k$ 温度量纲

52.

[答] $5.76 J\cdot K^{-1}\cdot mol^{-1}$

$\Delta S = R\ln[1/\sigma(CO)] - R\ln[1/\sigma(N_2)] = -R\ln(1/2)$

$= 5.76 J\cdot K^{-1}\cdot mol^{-1}$

53. [答] 分子平衡位置；分子振动基态能量。