

第七章 统计热力学

1. 设有一个由三个定位的单维简谐振子组成的系统,这三个振子分别在各自的位置上振动,系统的总能量为 $\frac{11}{2}h\nu$. 试求系统的全部可能的微观状态数.

解: $\epsilon_v = (v^{\text{①}} + \frac{1}{2})h\nu^{\text{②}}$

① ν 振动量子数.

② ν 振动频率.

	ν	0	1	2	3	4
	ϵ_v	$\frac{1}{2}h\nu$	$\frac{3}{2}h\nu$	$\frac{5}{2}h\nu$	$\frac{7}{2}h\nu$	$\frac{9}{2}h\nu$
(1)		1		2		
(2)		1	1		1	
(3)		2				1
(4)			2	1		

三个振子的总能量为 $\frac{11}{2}h\nu$, 上表为每个能级上分步的振子个数.

$$t_1 = \frac{3!}{1! 2!} = 3$$

$$t_2 = \frac{3!}{1! 1! 1!} = 6$$

$$t_3 = \frac{3!}{1! 2!} = 3$$

$$t_4 = \frac{3!}{1! 2!} = 3$$

$\Omega = t_1 + t_2 + t_3 + t_4 = 3 + 6 + 3 + 3 = 15$ 总共有 15 种可能的微观状态数.

2. 若有一个热力学系统,当其熵值增加 $0.418\text{J} \cdot \text{K}^{-1}$ 时,试求系统微观状态的增加数占原有微观状态数的比值(用 $\frac{\Delta\Omega}{\Omega_1}$).

解: 根据 $S = k \ln \Omega$ 则 $\Omega = \exp(S/k)$

$$\frac{\Delta\Omega}{\Omega} = \frac{\Omega_2 - \Omega_1}{\Omega_1} = \frac{\exp(S_2/k) - \exp(S_1/k)}{\exp(S_1/k)}$$

$$= \frac{\exp(S_2/k)}{\exp(S_1/k)} - 1 \approx \exp(\Delta S/k) = \exp\left(\frac{0.418}{1.38 \times 10^{-23}}\right) = \exp(3.03 \times 10^{22}).$$

3. 在海平面上大气的组成用体积分数可表示为: $\text{N}_2(\text{g})$ 为 0.78, $\text{O}_2(\text{g})$ 为 0.21, 其他气体为 0.01. 设大气中各气体都符合 Boltzmann 分布, 假设大气柱在整个高度内的平均温度为 220K. 试求: 这三类气体分别

在海拔 10km, 60km 和 500km 处的分压. 已知重力加速度为 $9.8 \text{ m} \cdot \text{s}^{-2}$.

解: 已知大气中气体符合 Boltzmann 分布, 则 $p = p_0 \exp\left(-\frac{mgh}{kT}\right) = p_0 \exp\left(-\frac{Mgh}{RT}\right)$

初始条件下: N_2 的分压为 $0.78p_0$; O_2 的分压为 $0.21p_0$; 其他气体为 $0.01p_0$ (设大气的总压为 p_0) $0.01 \times M_{\text{其他}} = M_{\text{空}} - M_{\text{N}_2} \times 0.78 - M_{\text{O}_2} \times 0.21$

海拔 10km 时, $M_{\text{其他}} = 44$

$$p'_{\text{N}_2} = 0.78p_0 \exp\left(-\frac{28 \times 10^{-3} \times 9.8 \times 10 \times 10^3}{8.314 \times 220}\right) = 0.1740p_0$$

$$p'_{\text{O}_2} = 0.21p_0 \exp\left(-\frac{32 \times 10^{-3} \times 9.8 \times 10 \times 10^3}{8.314 \times 220}\right) = 0.0378p_0$$

$$p'_{\text{其他}} = 0.01p_0 \exp\left(-\frac{44 \times 10^{-3} \times 9.8 \times 10 \times 10^3}{8.314 \times 220}\right) = 0.0009p_0$$

$$p'_{\text{总}} = p'_{\text{N}_2} + p'_{\text{O}_2} + p'_{\text{其他}} = 0.2127p_0$$

$$x'_{\text{N}_2} = \frac{p'_{\text{N}_2}}{p'_{\text{总}}} = 0.8181$$

$$x'_{\text{O}_2} = \frac{p'_{\text{O}_2}}{p'_{\text{总}}} = 0.1777$$

$$x'_{\text{其他}} = \frac{p'_{\text{其他}}}{p'_{\text{总}}} = 0.0042$$

同理, 海拔 60km 处

$$p'_{\text{N}_2} = 9.61 \times 10^5 p_0 \quad x'_{\text{N}_2} = 0.9307$$

$$p'_{\text{O}_2} = 7.15 \times 10^{-6} p_0 \quad x'_{\text{O}_2} = 0.0692$$

$$p'_{\text{其他}} = 7.19 \times 10^{-9} p_0 \quad x'_{\text{其他}} = 0.0001$$

海拔 500km 处

$$p'_{\text{N}_2} = 2.0677 \times 10^{-33} p_0 \quad x'_{\text{N}_2} = 0.999994$$

$$p'_{\text{O}_2} = 1.2354 \times 10^{-38} p_0 \quad x'_{\text{O}_2} = 0.000006$$

$$p'_{\text{其他}} = 6.4300 \times 10^{-54} p_0 \quad x'_{\text{其他}} \text{ 由于所含量过少, 可忽略不计.}$$

4. 对于双原子气体分子, 设基态振动能为零, $e^x \approx 1 + x$. 试证明

(1) $U_r = NkT$; (2) $U_v = NkT$.

证明: (1) $q_r = \frac{8\pi^2 IkT}{\sigma h^2}$

$$U_r = NkT^2 \left(\frac{\partial \ln q_r}{\partial T} \right)_{V, N} = NkT^2 \left[\frac{\partial}{\partial T} \left(\ln \frac{8\pi^2 IkT}{\sigma h^2} \right) \right]_{V, N} = NkT$$

证明: (2) 已知基态的振动能为零. $q_v = \frac{1}{1 - \exp\left(-\frac{h\nu}{kT}\right)}$

$$\begin{aligned} U_v &= NkT^2 \left(\frac{\partial \ln q_v}{\partial T} \right)_{V, N} \\ &= NkT^2 \left\{ \frac{\partial}{\partial T} \left[\ln \frac{1}{1 - \exp\left(-\frac{h\nu}{kT}\right)} \right] \right\}_{V, N} \\ &= \frac{N h \nu}{e^{h\nu/kT} - 1} \end{aligned}$$

已知 $e^x \approx 1 + x$, 则 $e^{h\nu/kT} \approx 1 + \frac{h\nu}{kT}$

$$U_v = NkT$$

5. 设某分子的一个能级的能量和简并度分别为 $\epsilon_1 = 6.1 \times 10^{-21}$, $g_1 = 3$, 另一个能级的能量和简并度分别为 $\epsilon_2 = 8.4 \times 10^{-21}$ J, $g_2 = 5$. 请分别计算在 300K 和 3000K 时, 这两个能级上分布的粒子数之比 N_1/N_2 .

$$\begin{aligned} \text{解: (1) 300K 条件下 } \frac{N_1}{N_2} &= \frac{g_1 e^{-\epsilon_1/kT}}{g_2 e^{-\epsilon_2/kT}} = \frac{g_1}{g_2} \exp[-(\epsilon_1 - \epsilon_2)/kT] \\ &= \frac{3}{5} \exp[-(6.1 - 8.4) \times 10^{-21} \text{ J} / 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \times 300 \text{ K}] \\ &= 1.05 \end{aligned}$$

(2) 3000K 条件下

$$\begin{aligned} \frac{N_1}{N_2} &= \frac{g_1}{g_2} \exp[-(\epsilon_1 - \epsilon_2)/kT] \\ &= \frac{3}{5} \exp[-(6.1 - 8.4) \times 10^{-21} \text{ J} / 1.38 \times 10^{-23} \cdot \text{K}^{-1} \times 3000 \text{ K}] = 0.63 \end{aligned}$$

6. 设有一个由极大数目的三维平动子组成的粒子系统, 运动于边长为 a 的立方容器内, 系统的体积、粒子质量和温度的关系为: $\frac{h^2}{8ma^2} = 0.10kT$. 现有两个能级的能量分别为: $\epsilon_1 = \frac{9h^2}{4ma^2}$, $\epsilon_2 = \frac{27h^2}{8ma^2}$, 试求处于这两个能级上粒子数的比值 $\frac{N_1}{N_2}$.

$$\text{解: } \epsilon = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$\epsilon_1 = \frac{9h^2}{4ma^2} = 1.8kT \quad (\text{已知 } \frac{h^2}{8ma^2} = 0.1kT)$$

$$n_x^2 + n_y^2 + n_z^2 = 18$$

$$n_1, n_2, n_3 = \begin{bmatrix} 1 & 1 & 4 \\ 4 & 1 & 1 \\ 1 & 4 & 1 \end{bmatrix} \quad g_1 = 3$$

$$\epsilon_2 = \frac{27h^2}{8ma^2} = 2.7kT$$

$$n_x^2 + n_y^2 + n_z^2 = 27$$

$$n_1, n_2, n_3 = \begin{bmatrix} 1 & 1 & 5 \\ 5 & 1 & 1 \\ 3 & 3 & 3 \end{bmatrix} \quad g_2 = 4$$

$$\frac{N_1}{N_2} = \frac{g_1}{g_2} \cdot \exp[-(\epsilon_1 - \epsilon_2)/kT]$$

$$= \frac{3}{4} \exp[-(1.8kT - 2.7kT)/kT]$$

$$= 1.84.$$

7. 将 $N_2(g)$ 在电弧中加热, 从光谱中观察到, 处于振动量子数 $v=1$ 的第一激发态上的分子数 $N(v=1)$, 与处于振动量子数 $v=0$ 的基态上的分子数 $N(v=0)$ 之比为:

$$\frac{N(v=1)}{N(v=0)} = 0.26$$

已知 $N_2(g)$ 的震动频率为 $6.99 \times 10^{13} \text{ s}^{-1}$. 试计算

(1) $N_2(g)$ 的温度;

(2) $N_2(g)$ 分子的平动、转动和振动能量;

(3) 振动能量在总能量中所占的分数.

解: (1) 根据玻兹曼分布, 且 $g_i(v)=1$

$$\frac{N_v=1}{N_v=0} = \exp[-(\epsilon_1 - \epsilon_0)/kT] = \exp(h\nu/kT) = 0.26$$

因为 $v=1$

$$T = \frac{-h\nu}{k \ln 0.26} = \frac{-6.63 \times 10^{-34} \text{ J} \cdot \text{S} \times 6.99 \times 10^{13} \text{ S}^{-1}}{1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \ln 0.26} = 2493 \text{ K}$$

(2) 平动, 转动为经典自由度, 服从能量均分原理.

$$\epsilon_t = \frac{3}{2} RT = \frac{3}{2} \times 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 2493 \text{ K} = 31.09 \text{ kJ}$$

$$\epsilon_r = RT = 20.73 \text{ kJ}$$

$$\epsilon_v = RT^2 \left(\frac{\partial \ln q_v}{\partial T} \right)_{v,N}$$

$$= RT^2 \left\{ \frac{\partial}{\partial T} \ln \left[\frac{\exp\left(-\frac{h\nu}{2kT}\right)}{1 - \exp\left(-\frac{h\nu}{kT}\right)} \right] \right\}_{v,N}$$

$$= \frac{1}{2} R \frac{h\nu}{k} + \frac{R \frac{h\nu}{k}}{\exp(h\nu/kT) - 1} = 23.78 \text{ kJ}$$

$$(3) \frac{\epsilon_v}{\epsilon_t + \epsilon_r + \epsilon_v} = \frac{23.78}{31.09 + 20.73 + 23.78} = 31.46\%$$

8. 设有一个由极大数目三维平动子组成的粒子系统, 运动于边长为 a 的立方容器中, 系统的体积、粒子质量和温度之间的关系为:

$$\frac{h^2}{8ma^2} = 0.1 k_B T$$

试计算平动量子数为 1, 2, 3 和 1, 1, 1 两个状态上粒子分布数的比值.

解: 因为平动量子数为 1, 2, 3 对应的量子态为 $\Psi_{1,2,3}; \Psi_{1,3,2}; \Psi_{2,1,3}; \Psi_{2,3,1}; \Psi_{3,1,2}; \Psi_{3,2,1}$ 简并度为 $g_1=6$

$$\epsilon_1 = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ma^2} (1^2 + 2^2 + 3^2) = 1.4 kT$$

同理 $g_0=1$

$$\epsilon_0 = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2}{8ma^2} (1^2 + 1^2 + 1^2) = 0.3 kT$$

$$\frac{N_1}{N_0} = \frac{g_1 e^{-\epsilon_1/kT}}{g_0 e^{-\epsilon_0/kT}} (\text{代入数值求解}) = 6e^{-1.1} = 1.997.$$

9. 设某理想气体 A, 其分子的最低能级是非简并的, 取分子的基态作为能量零点, 相邻能级的能量为 ϵ , 其简并度为 2, 忽略更高能级.

(1) 写出 A 分子的总配分函数的表示式;

(2) 设 $\epsilon=kT$, 求出相邻两能级上最概然分子数之比 $\frac{n_1}{n_0}$ 的值;

(3) 设 $\epsilon=kT$, 试计算在 298K 时, 1mol A 分子气体的平均能量.

解: (1) A 分子的总配分函数的表示式:

$$q = \sum_i g_i \exp(-\epsilon_i/kT)$$

$$= g_0 \exp(-\epsilon_0/kT) + g_1 \exp(-\epsilon_1/kT)$$

$$=1+2\exp(-\epsilon/kT).$$

$$(2) \frac{n_1}{n_0} = \frac{g_1 \exp(-\epsilon_1/kT)}{g_0 \exp(-\epsilon_0/kT)} = \frac{2\exp(-\epsilon/kT)}{1}$$

$$\text{将 } \epsilon = kT \text{ 代入 } \frac{n_1}{n_0} = \frac{2}{e} = 0.74.$$

(3) 298K, 1mol A 分子的平均能量.

$$U = RT^2 \left(\frac{\partial \ln q}{\partial T} \right)_{V, N} = RT^2 \left[\frac{\partial \ln \frac{1}{2\exp(-\epsilon/kT)}}{\partial T} \right]_{V, N} = RT \frac{2e^{-1}}{1+2e^{-1}} = 1053.68 \text{ J} \cdot \text{mol}^{-1}.$$

10. (1) 某单原子理想气体的配分函数 q 具有的函数形式为 $q = Vf(T)$, 试导出理想气体的状态方程.

(2) 若该单原子理想气体的配分函数 q 的函数形式为 $q = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$, 试导出压力 p 和热力学能 U 的表示式, 以及理想气体的状态方程.

$$\begin{aligned} \text{解: (1) } p &= NkT \left(\frac{\partial \ln q}{\partial V} \right)_{N, T} \\ &= NkT \frac{1}{Vf(T)} \cdot f(T) \quad (q = Vf(T)) \\ &= \frac{NkT}{V} \end{aligned}$$

$\therefore pV = NkT = nRT$ 对 1mol 理想气体, $PV_m = RT$

$$\begin{aligned} (2) p &= NkT \left(\frac{\partial \ln q}{\partial V} \right)_{N, T} \quad \left(q = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \right) \\ &= NkT \left(\frac{h^2}{2\pi mkT} \right)^{\frac{3}{2}} \cdot \frac{1}{V} \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} = \frac{NkT}{V} \end{aligned}$$

同理 $pV = NkT = nRT$

$$\begin{aligned} U &= NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_{N, V} \\ &= NkT^2 \cdot \frac{3}{2T} \left[\left(\frac{\partial \ln q}{\partial T} \right)_{N, V} = \frac{3}{2} \cdot \frac{1}{T} \right] = \frac{3}{2} NkT \end{aligned}$$

11. 某气体的第一电子激发态比基态能量高 $400 \text{ kJ} \cdot \text{mol}^{-1}$, 试计算

(1) 在 300K 时, 第一电子激发态分子所占的分数;

(2) 若要使激发态分子所占的分数为 10%, 则这时的温度为多少?

解: (1) 300K 条件下.

$$\begin{aligned} \frac{N_1}{N} &= \frac{\exp(-\epsilon_1/kT)}{\exp(-\epsilon_0/kT) + \exp(-\epsilon_1/kT)} \\ &= \frac{1}{\exp(\Delta\epsilon/kT) + 1} \\ &= \frac{1}{\exp\left(\frac{400 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300 \text{ K}}\right) + 1} \quad (\text{计算过程中 } \exp(\Delta\epsilon/RT) \gg 1 \text{ 可忽略}) \\ &= 2.25 \times 10^{-70}. \end{aligned}$$

$$(2) \text{同理 } \frac{N_1}{N} = \frac{1}{\exp(\Delta\epsilon/RT) + 1} = 10\%$$

$$T = \frac{\Delta\epsilon}{R \ln[(1-0.1)/0.1]} = \frac{400 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \cdot \ln 9} = 2189 \text{ K}.$$

12. 在 300K 时, 已知 F 原子的电子配分函数 $q_e = 4.288$, 试求

(1) 标准压力下的总配分函数(忽略核配分函数的贡献);

(2) 标准压力下的摩尔熵值. 已知 F 原子的摩尔质量为 $M=18.988\text{g} \cdot \text{mol}^{-1}$.

解: (1) $q=q_n \cdot q_e \cdot q_t$ 已知忽略核配分函数的贡献, $q_e=4.288$

$$q=4.288 \cdot q_t=4.288 \left[\frac{(2\pi mkT)^{3/2}}{h^3} \cdot V \right].$$

$$(2) S_m^\circ = S_{e,m} + S_{t,m}$$

$$= Nk \ln q_e + R \ln \left\{ \frac{(2\pi mkT)^{3/2}}{Lh^3} \cdot V_m \right\} + \frac{5}{2} R$$

$$= R \left[\ln q_e + \frac{3}{2} \ln \frac{M}{\text{kg} \cdot \text{mol}^{-1}} + \frac{5}{2} \ln \frac{T}{\text{K}} - 1.165 \right]$$

$$= R \left[\ln 4.288 + \frac{3}{2} \ln 18.998 + \frac{5}{2} \ln 300 - 1.165 \right]$$

$$= 157.69 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

13. 零族元素氩(Ar)可看作理想气体, 相对分子质量为 40, 取分子的基态(设其简并度为 1)作为能量零点, 第一激发态(设其简并度为 2)与基态的能量能为 ϵ , 忽略其他高能级.

(1) 写出 Ar 分子的总的配分函数表示式;

(2) 设 $\epsilon=5kT$, 求在第一激发态上最概然分布的分子数占总分子数的百分数;

(3) 计算 1 mol Ar(g) 在标准状态下的统计熵值. 设 Ar 分子的核和电子的简并度为均等于 1.

解: (1) Ar 分子的总的配分函数表示式:

$$q = \sum_i q_i \cdot \exp(-\epsilon_i/kT) = g_0 \exp(-\epsilon_0/kT) + g_1 \exp(-\epsilon_1/kT)$$

$$\text{已知 } g_0=1, \epsilon_0=0; g_1=2, \epsilon_1=\epsilon \text{ 则上式 } q=1+2\exp(-\epsilon/kT).$$

$$(2) \frac{N_1}{N} = \frac{g_1 \exp(-\epsilon_1/kT)}{g_0 \exp(-\epsilon_0/kT) + g_1 \exp(-\epsilon_1/kT)} = \frac{1}{\frac{g_0 \exp[(\epsilon_1 - \epsilon_0)/kT]}{g_1} + 1}$$

$$\text{已知 } \epsilon_1=5kT$$

$$\frac{N_1}{N} = \frac{1}{\frac{\exp(5kT/kT)}{2} + 1} = 0.0133.$$

$$(3) S_{t,m} = R \ln \left\{ \frac{(2\pi mkT)^{3/2}}{Lh^3} \cdot V_m \right\} + \frac{5}{2} R$$

$$= R \left(\frac{3}{2} \ln M + \frac{5}{2} \ln T - 1.165 \right)$$

$$= R \left(\frac{3}{2} \ln 40 + \frac{5}{2} \ln 298 - 1.165 \right)$$

$$= 154.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

14. 设 Na 原子气体(设为理想气体)凝聚成一表面膜.

(1) 若 Na 原子可以在膜内自由运动(即二维平动), 试写出此凝聚过程的摩尔平动熵变的统计表达式;

(2) 若 Na 原子在膜内不能运动, 其凝聚过程的摩尔平动熵变的统计表达式又将如何?

解: (1) 此凝聚过程

$$\text{三维平动配分函数 } q_{t,3} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V$$

$$\text{三维平动熵 } S_{m,3} = R \left[\ln \frac{q_{t,3}}{L} + \frac{5}{2} \right]$$

$$\text{二维平动配分函数 } q_{t,2} = \frac{2\pi mkT}{h^2} \cdot A$$

$$\text{二维平动熵 } S_{m,2} = R \left[\ln \frac{q_{t,2}}{L} + 2 \right]$$

Na 原子由三维到二维

$$\Delta S = S_{m,2} - S_{m,3} = -R \left[\ln \left(\frac{2\pi kT}{h^2} \right)^{\frac{1}{2}} \frac{V}{A} + \frac{1}{2} \right].$$

(2) 假设 Na 原子在膜内不动, 则平动熵为零

$$\Delta S = 0 - S_{m,3} = -R \left[\ln \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}} V - \ln L + \frac{5}{2} \right].$$

15. 试分别计算转动、振动和电子能级间隔的 Boltzmann 因子 $\exp\left(-\frac{\Delta \epsilon}{kT}\right)$ 各为多少? 已知各能及间隔的值为: 电子能级间隔约为 $100kT$, 振动能级间隔约为 $10kT$, 转动能级间隔约为 $0.01kT$.

$$\text{解: 电子能级间隔约为 } 100kT. \exp\left(-\frac{\Delta \epsilon}{kT}\right) = \exp\left(-\frac{100kT}{kT}\right) = 3.72 \times 10^{-44}$$

$$\text{振动能级间隔约为 } 10kT. \exp\left(-\frac{\Delta \epsilon}{kT}\right) = \exp\left(-\frac{10kT}{kT}\right) = 4.54 \times 10^{-5}$$

$$\text{转动能级间隔约为 } 0.01kT. \exp\left(-\frac{\Delta \epsilon}{kT}\right) = \exp\left(-\frac{0.01kT}{kT}\right) = 0.99.$$

16. 设 J 为转动量子数, 取整数, 转动简并度为 $(2J+1)$. 在 $240K$ 时, $CO(g)$ 最可能出现的量子态的转动量子数 J 的值为多少? 已知 $CO(g)$ 的转动特征温度为 $\Theta_r = 2.8K$.

$$\text{解: } q_r = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{J(J+1)\Theta_r}{T}\right]$$

$$\frac{dq_r}{dJ} = \left[2 - (2J+1)^2 \frac{\Theta_r}{T} \right] \exp\left[-J(J+1)\frac{\Theta_r}{T}\right] = 0$$

$$2 - (2J+1)^2 \frac{\Theta_r}{T} = 0$$

$$J = \left(\sqrt{\frac{2T}{\Theta_r}} - 1 \right) \times \frac{1}{2} = \left(\sqrt{\frac{240K \times 2}{2.8K}} - 1 \right) \times \frac{1}{2} = 6 \quad (J \text{ 取整数}).$$

17. HBr 分子的核间平衡距离 $r = 0.1414nm$, 试计算

(1) HBr 的转动特征温度;

(2) 在 $298K$ 时, HBr 分子占据转动量子数 $J=1$ 的能级上的百分数;

(3) 在 $298K$ 时, HBr 理想气体的摩尔转动熵.

$$\text{解: (1) } \Theta_r = \frac{h^2}{8\pi^2 I k}$$

$$I = \left(\frac{m_1 m_2}{m_1 + m_2} \right) r^2 = \frac{M_1 M_2}{M_1 + M_2} \cdot \frac{r^2}{L}$$

$$= \frac{1kg \cdot mol^{-1} \times 80kg \cdot mol^{-1} \times 10^{-6}}{(1+80)kg \cdot mol^{-1}} \times \frac{(0.1414 \times 10^{-9}m)^2}{6.02 \times 10^{23}mol^{-1}} = 3.28 \times 10^{-47}kg \cdot m^2$$

将数值代入转动特征温度 Θ_r 表达式

$$\Theta_r = \frac{(6.62 \times 10^{-34}J \cdot s)^2}{8 \times 3.14^2 \times 3.28 \times 10^{-47}kg \cdot m^2 \times 1.38 \times 10^{-23}J \cdot K^{-1}} = 12.3K.$$

(2) 异核双原子分子 $J=1$

$$q_r = \frac{T}{\Theta_r} = \frac{298K}{12.3K} = 24.23$$

$$\frac{N_1}{N} = \frac{(2J+1)e^{-J(J+1)\Theta_r/T}}{g} = \frac{3e^{-2\Theta_r/T}}{g} = \frac{3\exp(-2 \times 12.3/298)}{24.23} = 11.4\%.$$

$$(3) S_{m,r} = R \left(\ln \frac{2T}{\sigma} + 105.64 \right) = R \left(\ln \frac{3.28 \times 10^{-47} \times 298}{1} + 105.64 \right) = 34.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

18. 已知 H_2 和 I_2 的摩尔质量、转动特征温度和振动特征温度分别为：

物质	$M/(\text{kg} \cdot \text{mol}^{-1})$	Θ_r/K	Θ_v/K
H_2	2.0×10^{-3}	85.4	6100
I_2	253.8×10^{-3}	0.054	310

试求在 298K 时

(1) H_2 和 I_2 分子的平动摩尔热力学能，转动摩尔热力学能和振动摩尔热力学能；

(2) H_2 和 I_2 分子的平动定容摩尔热容，转动定容摩尔热容，振动定容摩尔热容和总的定容摩尔热容（忽略电子和核运动对热容的贡献）。

解：298K 的条件下

$$\begin{aligned} (1) U_r &= NkT^2 \left(\frac{\partial \ln q_r}{\partial T} \right)_{N,V} \\ &= NkT^2 \left[\frac{\partial}{\partial T} \left(\ln \frac{8\pi^2 I k T}{\sigma h^2} \right) \right]_{V,N} \\ &= NkT = RT = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{ K} = 2477.57 \text{ J} \cdot \text{mol}^{-1}. \end{aligned}$$

$$\begin{aligned} U_t &= NkT^2 \left(\frac{\partial \ln q_t}{\partial T} \right)_{V,N} \\ &= NkT^2 \left[\frac{\partial}{\partial T} \left(\ln \frac{2\pi m k T}{h^2} \right)^{3/2} V \right]_{V,N} \\ &= \frac{3}{2} NkT = \frac{3}{2} RT = 3716.36 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} U_v &= NkT^2 \left(\frac{\partial \ln q_v}{\partial T} \right)_{V,N} \\ &= NkT^2 \left\{ \frac{\partial}{\partial T} \left[\ln \frac{1}{1 - \exp(-\frac{h\nu}{kT})} \right] \right\}_{V,N} \\ &= \frac{Nh\nu}{e^{h\nu/kT} - 1} \quad (\Theta_v = \frac{h\nu}{k}) \\ &= \frac{N\Theta_v \cdot k}{\exp(\Theta_v/T) - 1} \\ &= \frac{R\Theta_v}{\exp(\Theta_v/T) - 1}. \end{aligned}$$

$$(2) C_{v,m,t} = \left(\frac{\partial U_t}{\partial T} \right)_v = \frac{3}{2} R = 12.47 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{v,m,r} = \left(\frac{\partial U_r}{\partial T} \right)_v = R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{v,m,v} = \left(\frac{\partial U_v}{\partial T} \right)_v$$

$$= 3Nk \left(\frac{h\nu}{kT} \right)^2 \frac{\exp(-\frac{h\nu}{kT})}{[\exp(-\frac{h\nu}{kT}) - 1]^2} = 3Nk \left(\frac{\Theta_v}{T} \right)^2 \frac{\exp(-\Theta_v/T)}{[\exp(-\Theta_v/T) - 1]^2}$$

$$C_{v,m} = C_{v,m,t} + C_{v,m,r} + C_{v,m,v}$$

$$\text{H}_2 \text{ 分子 } U_{m,t}=3716.36\text{J} \cdot \text{mol}^{-1}$$

$$U_{m,r}=2477.57\text{J} \cdot \text{mol}^{-1}$$

$$U_{m,v}=6.53 \times 10^{-5}\text{J} \cdot \text{mol}^{-1}$$

$$C_{V,m,t}=12.47\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m,r}=8.31\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m,v}=1.35 \times 10^{-5}\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m}=20.78\text{J} \cdot \text{mol}^{-1}$$

$$\text{F}_2 \text{ 分子 } U_{m,t}=3716.36\text{J} \cdot \text{mol}^{-1}$$

$$U_{m,r}=2477.57\text{J} \cdot \text{mol}^{-1}$$

$$U_{m,v}=1408.40\text{J} \cdot \text{mol}^{-1}$$

$$C_{V,m,t}=12.47\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m,r}=8.31\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m,v}=22.81\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m}=43.59\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

19. 在 298K 和 100kPa 时, 1 mol $\text{O}_2(\text{g})$ (设为理想气体) 放在体积为 V 的容器中, 试计算

(1) $\text{O}_2(\text{g})$ 的平动配分函数 q_t ;

(2) $\text{O}_2(\text{g})$ 的转支配分函数 q_r , 已知其核间距为 0.1207nm;

(3) $\text{O}_2(\text{g})$ 的电子配分函数 q_e , 已知电子基态的简并度为 3. 忽略电子激发态和振动激发态的贡献;

(4) $\text{O}_2(\text{g})$ 的标准摩尔熵值.

$$\text{解: (1) } m = \frac{M}{N_A} = \frac{32 \times 10^{-3} \text{kg} \cdot \text{mol}^{-1}}{6.02 \times 10^{23} \text{mol}^{-1}} = 5.31 \times 10^{-26} \text{kg}$$

$$V_m = \frac{RT}{p} = \frac{8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 298 \text{K}}{100 \times 10^3 \text{Pa}} = 0.0248 \text{m}^3 \cdot \text{mol}^{-1}$$

$$q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V = 4.34 \times 10^{30}.$$

$$(2) I = \frac{m_1 m_2}{m_1 + m_2} r^2 \text{ (同核双原子分子)} = \frac{m}{2} r^2 = 3.86 \times 10^{-46} \text{kg} \cdot \text{m}^2$$

$$q_r = \frac{8\pi^2 IkT}{2h^2} = 143.2.$$

$$(3) q_e = g_0 \cdot e = 3.$$

$$(4) S_{m,t} = R \left(\frac{3}{2} \ln M + \frac{5}{2} \ln T - 1.165 \right)$$

$$= 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \left(\frac{3}{2} \ln 32 + \frac{5}{2} \ln 298 - 1.1651 \right)$$

$$= 151.95 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_{m,r} = R \left(\ln \frac{IT}{\sigma} + 105.64 \right)$$

$$= 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \left(\ln \frac{3.86 \times 10^{-46} \times 298}{4} + 105.54 \right)$$

$$= 43.91 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_{m,e} = R \ln g_0$$

$$= 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \ln 3$$

$$= 9.13 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_m^\circ = S_{m,t} + S_{m,r} + S_{m,e}$$

$$= (151.95 + 43.91 + 9.13) \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 204.99 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

20. 在 298K 和 100kPa 时, 求 1 mol $\text{NO}(\text{g})$ (设为理想气体) 的标准摩尔熵值. 已知 $\text{NO}(\text{g})$ 的转动特征温度为 2.42K, 振动特征温度为 2690K, 电子基态与第一激发态的简并度均为 2, 两能级间的能量差为 $\Delta \epsilon = 2.473 \times 10^{-21} \text{J}$.

$$\text{解: } m = \frac{M}{N_A} = \frac{30 \text{kg} \cdot \text{mol}^{-1} \times 10^{-3}}{6.02 \times 10^{23} \text{mol}^{-1}} = 4.98 \times 10^{-26} \text{kg}$$

$$S_{t,m}^{\circ} = R \ln \left[\frac{3}{2} \ln M + \frac{5}{2} \ln T - 1.165 \right]$$

$$= 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \ln \left[\frac{3}{2} \ln 30 + \frac{5}{2} \ln 298 - 1.165 \right]$$

$$= 151.27 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$S_{r,m}^{\circ} = R \left(\ln \frac{T}{\sigma \Theta_r} + 1 \right)$$

$$= 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \left(\ln \frac{298}{1 \times 2.42} + 1 \right)$$

$$= 48.34 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_{v,m}^{\circ} = R \Theta_v T^{-1} (e^{\Theta_v/T} - 1)^{-1} - R \ln(1 - e^{-\Theta_v/T})$$

$$= 0.01 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_{e,m}^{\circ} = R \ln q^{\circ} + RT \ln \left(\frac{\partial \ln q^{\circ}}{\partial T} \right)_{V,N}$$

$$q_e = g_{e,0} + g_{e,1} \exp \left[-\frac{(\epsilon_1 - \epsilon_0)}{kT} \right] = 2 + 2e^{-\Delta \epsilon / kT}$$

$$S_{e,m}^{\circ} = R \ln(2 + 2e^{-179.2 \text{ K}/T}) + R \frac{2e^{(-179.2 \text{ K}/T)} \times T}{2(1 + e^{-179.2 \text{ K}/T}) T}$$

$$= R(1.130 + 0.213) = 11.166 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S_m^{\circ}(\text{NO} \cdot g) = 210.65 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

21. 在 298K 和 100kPa 时, 求 1 mol NO(g) (设为理想气体) 的标准摩尔残余熵值和标准摩尔量热熵值. 由 20 题算出的是统计熵值. 已知 NO(s) 晶体是 N₂O₂ 二聚分子级成, 在晶格中有两种排列方式.

$$\text{解: } S_{\text{残}} = \frac{1}{2} R \ln 2 = 2.88 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

量热熵是以绝对零度时晶体内部的熵值, 统计熵大于量热熵, 两者之间的差值为残余熵.

$$S_{\text{量}} = S_m^{\circ} - S_{\text{残}}$$

$$= 210.65 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - 2.88 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$= 207.77 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

22. 在 298K 和 100kPa 时, 求 1 mol SO₂(g) (设为理想气体) 的标准摩尔热力学能、焓、Gibbs 自由能、Helmholtz 自由能、熵、定压摩尔热容和定容摩尔热容等热力学函数. 已知 SO₂(g) 的摩尔质量为 $M(\text{SO}_2) = 64.063 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$, $\sigma_1 = 1151.4 \text{ cm}^{-1}$, $\sigma_2 = 517.7 \text{ cm}^{-1}$, $\sigma_3 = 1361.8 \text{ cm}^{-1}$; 三个转动惯量分别为: $I_x = 1.386 \times 10^{-46} \text{ kg} \cdot \text{m}^2$, $I_y = 8.143 \times 10^{-46} \text{ kg} \cdot \text{m}^2$, $I_z = 9.529 \times 10^{-46} \text{ kg} \cdot \text{m}^2$. SO₂(g) 分子的对称数为 2, 忽略电子和核的贡献.

$$\text{解: } A_{m,t} = kT \ln \frac{q_t^N}{N!}$$

$$q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V = 1.214 \times 10^{31}$$

$$A_{m,t} = -44.150 \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_{m,t} = k \ln \frac{q_t^N}{N!} + kT \left(\frac{\partial \ln q_t^N}{\partial T} \right)_{V,N} = 160.62 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$A = U - TS \quad H = U + nRT$$

$$\therefore U_{m,t} = A_{m,t} + TS_{m,t} = 3716.36 \text{ J} \cdot \text{mol}^{-1}$$

$$H_{m,t} = U_{m,t} + RT = 6194.2 \text{ J} \cdot \text{mol}^{-1}$$

$$C_{V,m,t} = \frac{3}{2}R = 12.47 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{p,m,t} = C_{V,m,t} + R = 20.785 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$G_{m,t} = A_{m,t} + RT = -41670 \text{ J} \cdot \text{mol}^{-1}$$

$$q_r = \frac{8\pi^2 (2\pi kT)^{3/2}}{\sigma h^3} (I_x I_y I_z)^{1/2} = 5847$$

$$A_{m,r} = G_{m,r} = -NkT \ln q_r = -RT \ln q_r = -21.48 \text{ kJ} \cdot \text{mol}^{-1}$$

$$S_{m,r} = - \left(\frac{\partial A_{m,r}}{\partial T} \right)_{V,N} = 84.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$H_{m,r} = U_{m,r} = TS_{m,r} + A_{m,r} = 3716.37 \text{ J} \cdot \text{mol}^{-1}$$

$$C_{p,m,r} = C_{V,m,r} = \frac{3}{2}R = 12.47 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$q_r = \prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-h\nu_i/kT)} = 1.095$$

$$A_{m,v} - H_{m,0,v} = G_{m,v} - H_{m,0,v} = -244.85 \text{ J} \cdot \text{mol}^{-1}$$

$$S_{m,v} = 2.867 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$H_{m,v} - H_{m,0,v} = U_{m,v} - H_{m,0,v} = 629.22 \text{ J} \cdot \text{mol}^{-1}$$

$$C_{p,m,v} = C_{V,m,v} = 6.559 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$\text{则: } U_m - H_{m,0,v} = 8061.94 \text{ J} \cdot \text{mol}^{-1}$$

$$H_m - H_{m,0,v} = 10539.78 \text{ J} \cdot \text{mol}^{-1}$$

$$G_m - H_{m,0,v} = -63384.85 \text{ J} \cdot \text{mol}^{-1}$$

$$A_m - H_{m,0,v} = -65964.8 \text{ J} \cdot \text{mol}^{-1}$$

$$S_m = 248.12 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{V,m} = 31.50 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$C_{p,m} = 39.81 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.$$

23. 计算 298K 时 HI, H₂, I₂ 的标准 Gibbs 自由能函数. 已知 HI 的转动特征温度为 9.0K, 振动转动特征温度为 3200K, 摩尔质量为 $M(\text{HI}) = 127.9 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$. I₂ 在零点时的总配分函数为 $q_0(\text{I}_2) = q_{t,0}$, $q_{r,0}$, $q_{v,0} = 4.143 \times 10^{35}$, H₂ 在零点时的总配分函数为 $q_0(\text{H}_2) = q_{t,0}$, $q_{r,0}$, $q_{v,0} = 1.185 \times 10^{29}$.

$$\text{解: HI 分子的质量 } m = \frac{127.9 \times 10^{-3}}{6.02 \times 10^{23}} = 2.12 \times 10^{-25} \text{ kg}$$

$$V_m = \frac{RT}{p} = \frac{8.314 \times 298}{10^5} = 0.0248 \text{ m}^3$$

$$q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \cdot V = 3.46 \times 10^{31}$$

$$A_{t,m} = -kT \ln \frac{q_t^N}{N!} = -RT(\ln q_t - \ln N + 1) \quad (N = 6.02 \times 10^{23}) = -41788.87 \text{ J} \cdot \text{mol}^{-1}$$

$$G_{t,m} = A_{t,m} + pV = -39311.29 \text{ J} \cdot \text{mol}^{-1}$$

$$q_r = \frac{8\pi^2 IkT}{h^2} = \frac{T}{\Theta_r} = 33.11$$

$$A_{r,m} = G_{r,m} = -RT \ln q_r = -8671.77$$

$$q_v = \frac{\exp[-\Theta_v/(2T)]}{1 - \exp(-\Theta_v/T)} = 4.66 \times 10^{-3}$$

$$A_{v,m} = G_{v,m} = -RT \ln q_v = 13302.35$$

$$G_m = G_{t,m} + G_{v,m} + G_{v,m} = -34680.71$$

$$I_2 \text{ 在零点时的总配分函数为 } q_0(I_2) = q_{t,0} q_{r,0} q_{v,0} = 4.143 \times 10^{35}$$

$$A_m = -kT \ln \frac{q^N}{N!} = -kT(\ln q - \ln N + 1) = -70009.6 \text{ J} \cdot \text{mol}^{-1}$$

$$G_m = -67532.1 \text{ J} \cdot \text{mol}^{-1}$$

$$\text{同理 } H_2 \quad G_m = -30202.0 \text{ J} \cdot \text{mol}^{-1}.$$

24. 计算 298K 时 HI, H_2, I_2 的标准热焓函数. 已知 HI, H_2, I_2 的振动转动特征温度分别为: 3200K, 6100K 和 610K.

$$\text{解: } \frac{H_m^\circ(T) - U_m^\circ(O)}{T} = RT \left(\frac{\partial \ln q}{\partial T} \right)_{v,N} + R$$

双原子分子基态的振动能量为零时, 振动配分数.

$$q_v = \frac{1}{1 - \exp(-\Theta_v/T)}$$

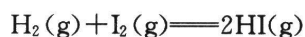
$$\frac{H_m^\circ(T) - U_m^\circ(O)}{T} = \frac{R\Theta_v/T}{\exp(\Theta_v/T) - 1} + R$$

则 HI 的标准热焓函数为: 8.3159

H_2 的标准热焓函数为: 8.314

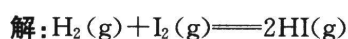
I_2 的标准热焓函数为: 10.8374.

25. 计算 298K, 时如下反应的标准摩尔 Gibbs 自由能变化值和标准平衡常数.



已知 398K 时, HI, H_2, I_2 的有关数据如下:

物质	$\frac{(G_{m,T}^\circ - H_{m,0K}^\circ)/T}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{(H_{m,T}^\circ - H_{m,0K}^\circ)/T}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	$\frac{\Delta_f H_{m,T}^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$
$H_2(g)$	-101.34	29.099	0
$I_2(g)$	-226.61	33.827	62.438
$2HI(g)$	-177.67	29.101	26.5



$$\sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} = [(-177.67) \times (-101.34) - (226.61)] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -27.39 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\sum_B \nu_B \left\{ \frac{H_m^\circ(T) - H_m^\circ(0)}{T} \right\} = [2 \times 29.101 - 29.099 - 33.827] \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = -4.724 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_{m(T)}^\circ = (2 \times 26.5 - 62.438 - 0) \times 10^3 \text{ J} \cdot \text{mol}^{-1} = -9.438 \times 10^3 \text{ J} \cdot \text{mol}^{-1}$$

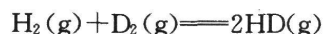
$$\begin{aligned} \Delta_r H_{m(0)}^\circ &= \Delta_r H_{m,T}^\circ - T \cdot \sum_B \nu_B \left\{ \frac{H_m^\circ(T) - H_m^\circ(0)}{T} \right\} \\ &= -9.438 \times 10^3 \text{ J} \cdot \text{mol}^{-1} - 298 \text{ K} \times (-4.724 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = -8030.25 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} -R \ln K^\circ &= \sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} + \frac{\Delta_r H_{m(0)}^\circ}{T} \\ &= -27.39 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \frac{-8030.25 \text{ J} \cdot \text{mol}^{-1}}{298 \text{ K}} \\ &= -54.347 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

$$K^\circ = 690.08$$

$$\begin{aligned}\Delta G_m, 298K &= T \times \sum_B \nu_B \frac{G_m^\circ(T) + H_m^\circ(D)}{T} + \Delta_r H_m^\circ(0) \\ &= 298K \times (-27.39J \cdot \text{mol}^{-1} \cdot K^{-1}) + (-8030.25J \cdot \text{mol}^{-1}) \\ &= -16.19 \times 10^3 J \cdot \text{mol}^{-1}.\end{aligned}$$

26. 计算 300K 时, 如下反应的标准平衡常数.

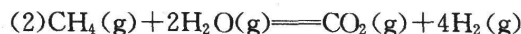
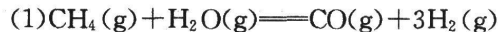


已知 298K 时, $\Delta U_m^\circ = 656.9J \cdot \text{mol}^{-1}$, HD, H_2 , D_2 的有关数据如下,

物理量	H_2	HD	D_2
$\sigma/(10^{-2}\text{cm}^{-1})$	4.371	3.786	3.092
$I/(10^{47}\text{kg} \cdot \text{m}^2)$	0.458	0.613	0.919

$$\begin{aligned}\text{解: } K &= \frac{[\text{HD}]^2}{[\text{H}_2][\text{D}_2]} = \frac{f_{\text{HD}}^2}{f_{\text{H}_2} f_{\text{D}_2}} \exp\left(-\frac{\Delta_r U_m^\circ(0)}{kT}\right) \\ &= \left(\frac{m_{\text{HD}}^2}{m_{\text{H}_2} m_{\text{D}_2}}\right)^{3/2} \left(\frac{\sigma_{\text{H}_2} \sigma_{\text{D}_2}}{\sigma_{\text{HD}}^2}\right) \left(\frac{I_{\text{HD}}^2}{I_{\text{D}_2} I_{\text{H}_2}}\right) \exp\left(-\frac{\Delta_r U_m^\circ(0)}{kT}\right) \\ &= \left(\frac{3^2}{1 \times 2}\right)^{3/2} \left(\frac{4.37 \times 3.092}{3.786^2}\right) \left(\frac{0.613^2}{0.458 \times 0.919}\right) \exp\left(-\frac{\Delta_r U_m^\circ(0)}{kT}\right) \\ &= 8.04 \times \exp\left(-\frac{656.9}{RT}\right) \\ &= 6.18.\end{aligned}$$

27. 计算 298K 时, 如下两个反应的标准平衡常数.

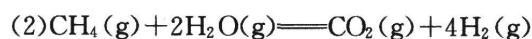


已知自由能函数和 0 K 时的焓变为:

函数	$\text{H}_2\text{O}(\text{g})$	$\text{CO}(\text{g})$	$\text{CO}_2(\text{g})$	$\text{CH}_4(\text{g})$	$\text{H}_2(\text{g})$
$-\frac{(G_{m,T}^\circ - H_{m,0K}^\circ)/T}{J \cdot K^{-1} \cdot \text{mol}^{-1}}$	155.56	168.41	182.26	152.55	102.17
$\frac{\Delta_f H_{m,0K}^\circ}{kJ \cdot \text{mol}^{-1}}$	-238.9	-113.81	-393.17	-66.90	0

解: (1) $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$

$$\begin{aligned}\sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} &= [(-168.41) + 3 \times (-102.17) - (-152.55) - (-155.56)] J \cdot K^{-1} \cdot \text{mol}^{-1} \\ &= -166.81 J \cdot K^{-1} \cdot \text{mol}^{-1} \\ \Delta_r H_m^\circ(0) &= [(-113.81) + 3 \times 0 - (-238.9) - (-66.90)] kJ \cdot \text{mol}^{-1} = 191.99 kJ \cdot \text{mol}^{-1} \\ -R \ln K^\circ &= \sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\}_B + \frac{\Delta_r H_m^\circ(0)}{T} \\ &= -166.81 J \cdot K^{-1} \cdot \text{mol}^{-1} + \frac{191.99 \times 10^3 J \cdot \text{mol}^{-1}}{298K} \\ &= 477.45 J \cdot K^{-1} \cdot \text{mol}^{-1} \\ K^\circ &= 1.15 \times 10^{-25}.\end{aligned}$$



$$\sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} \\ = [(-182.26) + 4 \times (-102.17) - (-152.55) - 2 \times (-155.56)] \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ = -127.27 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\circ(0) = [(-393.17) + 4 \times 0 - (-66.90) - 2 \times (-238.9)] \text{kJ} \cdot \text{mol}^{-1} \\ = 151.53 \text{kJ} \cdot \text{mol}^{-1}$$

$$-R \ln K^\circ = \sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\}_B + \frac{\Delta_r H_m^\circ(0)}{T} \\ = -127.27 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{151.53 \times 10^3 \text{J} \cdot \text{mol}^{-1}}{298 \text{K}} \\ = 381.22 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$K^\circ = 1.22 \times 10^{-20}$$

28. 计算 298K 时, 如下反应的标准平衡常数.



已知热力学数据如下表:

函数	CO(g)	H ₂ O(g)	CO ₂ (g)	H ₂ (g)
$\frac{\Delta_f H_{m,0K}^\circ}{\text{kJ} \cdot \text{mol}^{-1}}$	-110.52	-241.83	-393.51	0
$\frac{(H_{m,T}^\circ - U_{m,0K}^\circ)/T}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	29.09	33.20	31.41	28.48
$-\frac{(G_{m,T}^\circ - H_{m,0K}^\circ)/T}{\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}}$	168.82	155.53	182.23	102.19

解: 已知 0 K 时, $U_0 = H_0$; 根据书中所给 $\Delta_f H_{m,0K}^\circ$ 数据求

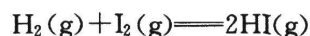
$$\Delta_r H_m^\circ(0) = [(-393.51) + 0 - (-110.52) - (-241.83)] \text{kJ} \cdot \text{mol}^{-1} \\ = -41.16 \text{kJ} \cdot \text{mol}^{-1}$$

$$\sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} = [(-182.23) + (-102.19) - (-168.82) - (155.53)] \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ = 39.93 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$-R \ln K^\circ = \sum_B \nu_B \left\{ \frac{G_m^\circ(T) - H_m^\circ(0)}{T} \right\} + \frac{\Delta_r H_m^\circ(0)}{T} \\ = 39.93 \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{-41.16 \times 10^3 \text{J} \cdot \text{mol}^{-1}}{298 \text{K}} \\ = -98.19$$

$$K^\circ = 1.35 \times 10^5$$

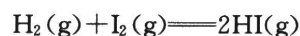
29. 用配分函数计算 298K 时, 如下反应的标准平衡常数.



已知反应的 $\Delta_r U_m^\circ(0) = -8.03 \text{kJ} \cdot \text{mol}^{-1}$, 在 298K 时的参数如表所示, 忽略电子和核的贡献.

分 子	$M/(\text{kg} \cdot \text{mol}^{-1})$	Θ_r/K	Θ_v/K
$\text{H}_2(\text{g})$	2.0×10^{-3}	85.4	6100
$\text{I}_2(\text{g})$	253.8×10^{-3}	0.054	310
$\text{HI}(\text{g})$	127.9×10^{-3}	9.0	3200

$$\text{解: } \Theta_r = \frac{h^2}{8\pi^2 Ik} \quad \Theta_v = \frac{h\nu}{k}$$



$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{f_{\text{HI}}^2}{f_{\text{H}_2} f_{\text{I}_2}} \exp\left(\frac{\Delta_r U_m^\circ(0)}{kT}\right)$$

$$= \left(\frac{g_{\text{HI}}^2}{g_{\text{H}_2} g_{\text{I}_2}}\right)_{\text{电子}} \left(\frac{m_{\text{HI}}^2}{m_{\text{H}_2} m_{\text{I}_1}}\right)^{3/2} \left(\frac{\sigma_{\text{H}_2} \sigma_{\text{I}_2}}{\sigma_{\text{H}_2}^2}\right) \left(\frac{I_{\text{H}_2}^2}{I_{\text{H}_2} I_{\text{I}_2}}\right) \cdot$$

$$\frac{\left[1 - \exp\left(-\frac{h\nu_{\text{H}_2}}{kT}\right)\right] \left[1 - \exp\left(-\frac{h\nu_{\text{I}_2}}{kT}\right)\right]}{\left[1 - \exp\left(-\frac{h\nu_{\text{HI}}}{kT}\right)\right]^2} \exp\left(-\frac{\Delta_r U_m^\circ(0)}{kT}\right)$$

$\text{HI}, \text{H}_1, \text{I}_2$ 的电子能级的简并度 g 均为 1

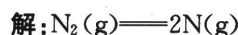
$$\sigma_{\text{HI}} = 1; \sigma_{\text{H}_2} = 2; \sigma_{\text{I}_2} = 2$$

$$K = \left(\frac{M_{\text{H}_2}}{M_{\text{H}_2} M_{\text{I}_2}}\right)^{3/2} \left(\frac{2 \times 2}{1^2}\right) \left(\frac{\Theta_{r, \text{H}_2} \cdot \Theta_{r, \text{I}_2}}{\Theta_{r, \text{HI}}^2}\right) \cdot \frac{\left[1 - \exp\left(-\frac{\Theta_{v, \text{H}_2}}{T}\right)\right] \left[1 - \exp\left(-\frac{\Theta_{v, \text{I}_2}}{T}\right)\right]}{\left[1 - \exp\left(-\frac{\Theta_{v, \text{HI}}}{T}\right)\right]^2}$$

$$\cdot \exp\left(-\frac{\Delta_r U_m^\circ(0)}{RT}\right) \quad (\text{将数值代入计算})$$

$$K = 688.32.$$

30. 计算 5000K 时, 反应 $\text{N}_2(\text{g}) \rightleftharpoons 2\text{N}(\text{g})$ 的标准平衡常数. 已知 $\text{N}_2(\text{g})$ 分子的转动特征温度 $\Theta_r = 2.84\text{K}$, 振动特征温度 $\Theta_v = 3350\text{K}$, 解离能 $D = 708.35\text{kJ} \cdot \text{mol}^{-1}$, $\text{N}_2(\text{g})$ 的电子基态是非简并的, 而 N 原子的基态是 4 度简并的.



$$K = \frac{g_{\text{N}}^2}{g_{\text{N}_2}} \cdot \left(\frac{m_{\text{N}}^2}{m_{\text{N}_2}}\right)^{3/2} \cdot \frac{\sigma_{\text{N}_2}}{\sigma_{\text{N}}} \cdot \frac{I_{\text{N}}^2}{I_{\text{N}_2}} \cdot \frac{1 - \exp\left(-\frac{h\nu_{\text{N}_2}}{kT}\right)}{\left[1 - \exp\left(-\frac{h\nu_{\text{N}}}{RT}\right)\right]^2} \exp\left(-\frac{\Delta_r U_m^\circ(0)}{kT}\right)$$

$$\text{已知 } g_{\text{N}_2} = 1 \quad g_{\text{N}} = 4$$

$$M_{\text{N}} = 14 \times 10^{-5} \text{kg} \cdot \text{mol}^{-1} \quad M_{\text{N}_2} = 28 \times 10^{-3} \text{kg} \cdot \text{mol}^{-1}$$

$$\sigma_{\text{N}} = 1 \quad \sigma_{\text{N}_2} = 2$$

$$I = \frac{h^2}{8\pi^2 k \Theta_r} \quad \Theta_r = \frac{h\nu}{k}$$

$$K = \frac{4^2}{1} \cdot \left(\frac{14^2 \times 10^{-6}}{28 \times 10^{-3} \times 6.02 \times 10^{23}}\right)^{3/2} \cdot \frac{2}{1} \cdot I \cdot \frac{1}{1 - \exp\left(-\frac{h\nu}{kT}\right)} \exp\left(\frac{\Delta_r U_m^\circ(0)}{RT}\right)$$

$$= 4.30 \times 10^{-78}.$$