6-13

1) $J_{max} = \frac{1}{2}\left[\frac{2T}{\theta_r}\right]^{1/2} - \frac{1}{2}$; $\theta_r = \frac{hc\widetilde{B}_e}{k}$

$\widetilde{B}_e = 1.9982\ cm^{-1} \Rightarrow \theta_r = 2.875\ K$

Sustituyendo T y θ_r en J_{max}

$J_{max} = \frac{1}{2}\left[\frac{2(300K)}{2.875K}\right]^{1/2} - \frac{1}{2} = 6.7231 \simeq 6.7 \simeq 7$

2) La fracción en $n>0$ es $e^{-\theta_r/T}$; $\theta_r = \frac{hc\,w_e}{k}$

Para N_2, $w_e = 2358.6\ cm^{-1}$

$\Rightarrow \theta_r = \frac{hc\,w_e}{k} = 3393\ K$

así que $\pi_{>0} = e^{-\theta_r/T} = e^{-3393/300} = 1.2\times10^{-5}$

Lo más probable es $n=0$ a $300°K$

Problema 4-8

Sol

Partiendo de la función de partición

- Para un boson o fermión, el gran ensamble canonico esta dado como

$$\left(S = k\ln\Theta + kT\left(\frac{\partial \ln}{\partial T}\right)_{T,\mu}\right) \quad \text{Donde} \quad \Theta = \prod_j \left(1 + \lambda e^{-\varepsilon_j/kT}\right)^{\pm 1}$$

$$\Rightarrow \ln\Theta = \pm\sum_j \left(1 + \lambda e^{-\varepsilon_j/kT}\right) \Rightarrow \frac{\partial \ln\Theta}{\partial T} = \pm\sum_j \frac{\frac{\partial \pm\lambda e^{-\varepsilon_j/kT}}{\partial T}}{1 \pm \lambda e^{-\varepsilon_j/kT}}$$

$$= \sum_j \frac{\left(\frac{\varepsilon_j - \mu}{kT^2}\right)\exp\left(\frac{-(\varepsilon_j - \mu)}{kT}\right)}{1 \pm \lambda e^{-\varepsilon_j/kT}} \Rightarrow S = k\sum_j \left\{ \pm\ln\left(1 \pm \lambda e^{-\varepsilon_j/kT}\right) + \frac{\lambda e^{-\beta\varepsilon_j}\left(\frac{\varepsilon_j - \mu}{kT}\right)}{1 \pm \lambda e^{-\beta\varepsilon_j}}\right.$$

Tomamos a $u = 1 \pm \lambda e^{-\beta\varepsilon_j}$ y $v = \lambda e^{-\beta\varepsilon_j}$

$$\Rightarrow u = 1 \pm v \text{ y } u \pm v = 1 \Rightarrow n_j = \frac{v}{u}$$

$$\Rightarrow S = k\sum_j \{\pm\ln u - \bar{n}_j \ln v\} = k\sum_j \{\pm\ln u - \bar{n}_j \ln\bar{n}_j - \bar{n}_j \ln u\}$$

$$= k\sum_j \left\{-(\pm 1 - \bar{n}_j)\ln\left(\frac{1}{u}\right) - \bar{n}_j \ln\bar{n}_j\right)$$ Renombrando $u \pm v = 1$

$$\boxed{S = -k\sum_j \left\{\bar{n}_j \ln\bar{n}_j \mp (1 \mp \bar{n}_j)\ln(1 \mp \bar{n}_j)\right)}$$

7.20

$v_0 = \sqrt{\gamma \frac{RT}{M}}$; usando $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$; $\gamma = \frac{5}{3}$

$$v_0 = \sqrt{\frac{5}{3}\frac{RT}{M}} = \sqrt{\frac{5}{3}\frac{RT}{M}\frac{8\pi}{8\pi}} =$$

$$\sqrt{\frac{8RT}{\pi M}\frac{5\pi}{24}} = \sqrt{\frac{5\pi}{24}}\,\bar{v} = \underline{0.81\bar{v}}$$

7.4:

Dado $P = \rho g z = \frac{m}{V} g z \rightarrow dP = -\frac{m}{V} g\, dz$ — (1)

Ahora por los de gases ideales. $PV = nRT \rightarrow PV = KT \rightarrow V = \frac{KT}{P}$

en (1) $dP = -\frac{mP}{KT} g\, dz \rightarrow \frac{dP}{P} = -\frac{mg}{KT} dz \xrightarrow{\text{integrando}} \ln P = -\frac{mg}{KT} z + \ln c$

$\rightarrow \ln\left(\frac{P}{c}\right) = -\frac{mg}{KT} z \rightarrow \frac{P}{c} = e^{-\frac{mgz}{KT}} \longrightarrow P = c\, e^{-\frac{mgz}{KT}} \rightarrow$ tomando $z=0$

$P = P_0 \longrightarrow P_0 = c \quad \therefore \quad \boxed{P = P(0)\, e^{-\frac{mgz}{KT}}}$

tomando lo más alto del monte Everest.

$P(0) = 760\, mmHg \longrightarrow$ masa molar $= 0.02896\, Kg/mol$

$R = 8.3143\, J/K{\cdot}mol \;;\; T = 273°K$

$g = 9.81\, m/s^2 \;;\; z = 8848\, m \longrightarrow$ Altura del Everest.

$P = P(0)\, e^{-\frac{Mgz}{KT}} \rightarrow M = \frac{m}{n} \rightarrow P = 760\, e^{-\frac{0.02896(9.81)(8848)}{8.3143(273)}}$

$\therefore \quad \boxed{P = 251.10\, mmHg}$

5-2

Entropia $S = \frac{3NK}{2}\left[1 + \ln\left(\frac{2N\pi V^{2/3}E}{h^2}\right)\right] \cdots (1)$

$\Rightarrow$ E = Energia Cinetica $\left(\frac{\partial S}{\partial E}\right) = \frac{1}{T} \cdots (2)$

Resolvemos $\left(\frac{\partial S}{\partial E}\right)_{mv} = \frac{3NK}{2} \times \frac{h^2}{2m\pi V^{2/3}} \times \frac{2m\pi V^{2/3}}{h^2} = \frac{3NK}{2}$

$$\frac{3NK}{2E} = \frac{1}{T} \Rightarrow E = \frac{3}{2}NKT$$

Entropia $A = ETP_V$: P_V = gas ideal = NKT

$$A = \frac{3}{2}NKT + NKT \Rightarrow A = \frac{5}{2}NKT$$

Calor Especifico a V = conts.

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{3}{2}\frac{\partial}{\partial T}(NKT) \Rightarrow C_V = \frac{3}{2}NK$$

Para el potencia Quimico(μ) $\left(\frac{\partial S}{\partial N}\right) = \frac{\mu}{T}$

5-2 2d2

Con (1)

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = \frac{3k}{2} + \frac{3k}{2} \ln\left(\frac{2\pi m V^{2/3} E}{h^2}\right) \cdots (3)$$

$$-\frac{\mu}{T} = \frac{3k}{2} + \frac{3k}{2} \ln\left(\frac{2\pi m V^{2/3} E}{h^2}\right)$$

$$\Rightarrow \mu = -\frac{3}{2} kT \left[1 + \ln(2\pi m^{2/3} E)\right]$$

Energia Libre de Gibbs $\Rightarrow G = A - TS$

$$G = \frac{5}{2} NkT - T \frac{3Nk}{2} \left[1 + \ln\left(\frac{2k m V^{2/3} E}{h^2}\right)\right]$$

$$G = NkT\left[\frac{5}{2} - \frac{3}{2}\left[\frac{2\pi m V^{2/3} E}{h^2}\right]\right]$$

7-8.

La constante de Botzmann se puede aproximar usando la relación dada en una sospensión coloidal de partículas en un campo gravitacional:

$$K_B = -\frac{mg(h-h_0)}{\ln(n/n_0)T} \; ; \quad \text{Sea } n=9,\ n_0=100,\ h=1\times10^{-4}\,m,\ h_0=0,\ m=1\times10^{-17} \text{ entonces}$$

$$K_B = \frac{9.8\times10^{-21}}{\ln(0.09)\cdot 300} \approx 1357\times10^{-23}\ \frac{m^2 kg}{s^2 K}$$

5.17)

Sea $\Delta(N, \varphi, T) = \left(\frac{KT}{\varphi\Lambda^3}\right)^N$

$$\Rightarrow G = -KT \ln \Delta$$
$$= -KT \ln\left(\frac{KT}{\varphi\Lambda^3}\right)^N$$
$$\Rightarrow G = -NKT \ln\left(\frac{KT}{\varphi\Lambda^3}\right)$$

Sabemos

$$G = U - TS + PV$$
$$\rightarrow dG = dU - TdS - SdT + PdV + VdP$$
$$= TdS - PdV - TdS - SdT + PdV + Vd\varphi$$
$$\therefore dG = -SdT + Vd\varphi$$
$$\Rightarrow S = -\frac{dG}{dT} = NKT\left(\frac{P\Lambda^3}{KT}\right) \cdot \frac{K}{P\Lambda^3} - NK\ln\left(\frac{KT}{P\Lambda^3}\right)$$
$$\Rightarrow S = NK\left[1 - \ln\left(\frac{KT}{\Lambda^3\varphi}\right)\right]$$

y $V = \frac{dG}{d\varphi} = -NKT\left(\frac{P\Lambda^3}{KT}\right)\left(\frac{KT}{P^2\Lambda^3}\right) \Rightarrow V = \frac{NKT}{P}$

7.32

$$H=\frac{1}{2m}\left(p_x^2+p_y^2\right)+\frac{k}{2}\left(x^2+y^2\right)$$

$$\Rightarrow \bar{E}=\int_{-\infty}^{\infty} e^{-\frac{H}{k_BT}} H\, d^2p\, d^2R=\int_{-\infty}^{\infty} e^{-\frac{H}{k_BT}}\, d^2p\, d^2R$$

$$=\frac{1}{2m}\left\{ 2m\left(\frac{1}{2}k_BT+\frac{1}{2}k_BT\right)+\frac{k}{2}\left(\frac{2}{k}\left(\frac{1}{2}k_BT+\frac{1}{2}k_BT\right)\right)\right.$$

$$=k_BT+k_BT=2k_BT$$

Si $x^2+y^2=R^2$

$x=R\cos\theta$

$y=R\sin\theta$

$$\Rightarrow H=\frac{1}{2}\left(m\left(v_x^2+v_y^2\right)\right)+\frac{k}{2}R^2$$

$$\Rightarrow \dot{x}=\dot{R}\cos\theta-R\sin\theta$$

$$\dot{y}=\dot{R}\sin\theta+R\cos\theta$$

$$\Rightarrow \dot{x}+\dot{y}=\dot{R}\left(\cos^2\theta+\sin^2\theta\right)+R^2\dot{\theta}^2\left(\cos^2\theta+\sin^2\theta\right)$$

$$=\dot{R}^2+R^2\dot{\theta}^2$$

$$\Rightarrow m\dot{R}=p_r \quad y \quad mR^2\dot{\theta}=p_\theta \Rightarrow \dot{r}=\frac{p_r}{m}$$

$$\dot{\theta}=\frac{p_\theta}{mR^2}$$

$$\Rightarrow H = \frac{1}{2} m \left(\dot{R}^2 + R^2 \dot{\theta}^2 \right) + \frac{k}{2} R^2 = \frac{1}{2} m \left(\frac{p_R^2}{m^2} + \frac{R^2 p_\theta^2}{m^2 R^4} \right) + \frac{k}{2} R^2$$

$$= \frac{1}{2m} \left(p_R^2 + \frac{p_\theta^2}{R^2} \right) + \frac{k}{2} R^2$$

$$\Rightarrow \bar{E} = \frac{\frac{1}{2m} \int_{-\infty}^{\infty} p_R^2 e^{-\frac{1}{2m} p_R^2} \, dp_R}{\int_{-\infty}^{\infty} e^{-\frac{1}{2m} p_R^2} \, dp_R} + \frac{\frac{1}{2mR^2} \int_{-\infty}^{\infty} p_\theta^2 e^{-\frac{1}{2mR^2} p_\theta^2} \, dp_\theta}{\int_{-\infty}^{\infty} e^{-\frac{1}{2mR^2} p_\theta^2} \, dp_\theta}$$

$$+ \frac{\frac{k}{2} \int_0^{\infty} R^2 e^{-\frac{k}{2} R^2} \, dR}{\int_0^{\infty} e^{-\frac{k}{2} R^2} \, dR} = \frac{1}{2} k_B T + \frac{1}{2} k_B T + k_B T$$

$$= 2 k_B T$$

4.5

Sea la presión

$$P = \frac{2}{3}\frac{E_{ke}}{V} \rightarrow PV = \frac{2}{3}E_{ke}$$

Para ke (Energía cinetica) en 3D

$$E = \frac{3}{2}nRT$$

Sustituimos E_{ke} en P

$$P \cdot V = \frac{2}{3} \cdot \frac{3}{2}\, nRT = nRT$$

$$\therefore P = \frac{nRT}{V} \rightarrow \text{Gas ideal}$$

ke directamente proporcional a P

4-18.

Para partículas independientes

$$E = N\bar{\varepsilon} = N\frac{\sum_j \varepsilon_j e^{-\varepsilon_j/kT}}{\sum_j e^{-\varepsilon_j/kT}}$$

Entonces C_V está dado por...

$$C_V = \frac{\partial E}{\partial T} = N\frac{\partial \bar{\varepsilon}}{\partial T} = N\frac{\partial}{\partial T}\frac{\sum_j \varepsilon_j e^{-\varepsilon_j/kT}}{\underbrace{\sum_j e^{-\varepsilon_j/kT}}_{q}}$$

$$= \frac{N}{q^2}\left[\sum_j \frac{\varepsilon_j}{kT^2}\varepsilon_j e^{-\varepsilon_j/kT}\cdot q - \left(\sum_j \frac{\varepsilon_j}{kT^2}e^{-\varepsilon_j/kT}\right)\left(\sum_j \varepsilon_j e^{-\varepsilon_j/kT}\right)\right]$$

$$= \frac{N}{kT^2}\left(\frac{\sum_j \varepsilon_j^2 e^{-\varepsilon_j/kT}}{q} - \left(\frac{\sum_j \varepsilon_j e^{-\varepsilon_j/kT}}{q}\right)^2\right)$$

$$= \frac{N}{kT^2}\left(\overline{\varepsilon^2} - \bar{\varepsilon}^2\right)$$

Para el gas ideal, $\sigma_\varepsilon^2 = \frac{kT^2}{N}Nk = k^2T^2 \Rightarrow \sigma_\varepsilon = kT$

y $\varepsilon = \frac{3}{2}kT$. Con lo que la fluctuación en la energía molecular es del mismo orden de la propia energía molecular y por lo tanto no es desprecrable.

7.6 La energia del gas $E = F + T_e$

Asumiendo el mov. clasico

$$F = -k_B T N \ln z_r \ ; \ z_r = \int e^{-\frac{\varepsilon_r}{k_B T}} \frac{dp\,d\theta\,dp_\theta\,dp_\phi}{(2\pi\hbar)^2}$$

$$\varepsilon_r = \frac{1}{2I}\left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta}\right) - \mu E \cos\theta$$

$$\therefore\ z = \frac{1}{(2\pi\hbar)^2}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_{-\infty}^{\infty} dP_\phi$$

$$\alpha \exp\left[-\frac{1}{2Ik_B T}\left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta}\right) + a\cos\theta\right.$$

$$z_r = \frac{I k_B T}{\hbar^2}\int_0^{\pi} e^{a\cos\theta}\,\text{sen}\,\theta\, d\theta$$

Sea $x = \cos\theta$; $z_R = \frac{2I k_B T}{\hbar^2}\cdot\frac{\text{Sh}\,a}{a}$

$$\therefore F_R = -k_B T N\left[\ln\left(\frac{\text{Sh}\,a}{a}\right) + \ln\left(\frac{2I k_B T}{\hbar^2}\right)\right]$$

$$\Rightarrow F = -k_B N T\left[\ln\left(\frac{e}{N} z_t\right) + \ln z_r\right]$$

La entropia es: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,E}$

$$S(0) = \frac{5}{2}k_B N + k_B N\left[\ln\left(\frac{eV}{N\hbar^3}\right)\left(\frac{M k_B T}{2\pi}\right)^{3/2}\right] + k_B N \ln\left(\frac{2I k_B T}{\hbar^2}\right)$$

Para $\mathcal{E}$ pequeño

$$a\,l(a) - \ln sh\,a \quad \frac{\ln sh\,a}{a} = \frac{a^2}{6} = \frac{1}{6}\left(\frac{\mu\mathcal{E}}{k_B T}\right)^2$$

$$E = F + TS = \frac{5}{2} k_B NT - N\mu\mathcal{E} L(a)$$

$$E = \frac{5}{2} k_B NT - \frac{1}{3} k_B NT \left(\frac{\mu\mathcal{E}}{k_B T}\right)^2$$

La capacidad calorífica $\quad C_v = \left(\frac{\partial E}{\partial T}\right)_v$

$$= \frac{5}{2} k_B N - N\mu\mathcal{E} \frac{dL(a)}{da} \frac{da}{dT}$$

Para $\mathcal{E}$ pequeño

$$a\,l(0) - \frac{\ln sh\,a}{a} = \frac{a^2}{6} = \frac{1}{6}\left(\frac{\mu\mathcal{E}}{k_B T}\right)^2$$

$$E = F + TS = \frac{5}{2} k_B N T - N\mu\mathcal{E}\,L(a)$$

$$E = \frac{5}{2} k_B N T - \frac{1}{3} k_B N T\left(\frac{\mu\mathcal{E}}{k_B T}\right)^2$$

La capacidad calorífica $C_v = \left(\frac{\partial E}{\partial T}\right)_v$

$$= \frac{5}{2} k_B N - N\mu\mathcal{E}\,\frac{dL(a)}{da}\,\frac{da}{dT}$$