

A) $g_E = 2 + 1 e^{-\beta 0.05 \text{ eV}}$

$$P(2) = 0.1 = \frac{1 e^{-\beta \epsilon_2}}{2 + e^{-\beta \epsilon_2}} \rightarrow 0.2 + 0.1 e^{-\beta \epsilon_2} = e^{-\beta \epsilon_2}$$

$$0.2 = 0.9 e^{-\beta \epsilon_2}$$

$$\ln \frac{0.2}{0.9} = -\beta \epsilon_2$$

$$k_B T = \frac{1}{\beta} = \frac{1}{\epsilon_2} \ln \frac{0.9}{0.2}$$

$$T = \frac{1}{k_B \epsilon_2} \ln \frac{0.9}{0.2}$$

$$T = \left(\frac{1}{\frac{1.38 \times 10^{-23} \text{ J/K}}{1.602 \times 10^{-19} \text{ J/eV}} \cdot 0.05 \text{ eV}} \right) \ln \frac{0.9}{0.2}$$

$$T = 3.5 \times 10^5 \text{ K}$$

B) $\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$

$$\ln Q = N \ln(V-b) - \ln N! + \frac{3N}{2} \ln \left(\frac{2\pi m k_B}{h^2} \right) + \frac{3N}{2} \ln T$$

T in only last term

(a) $\langle E \rangle = k_B T^2 \frac{\partial}{\partial T} \left(\frac{3N}{2} \ln T \right)_{N,V}$

$$= \frac{3N}{2} k_B T^2 \left(\frac{1}{T} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

$$N_A n = N, N_A k_B = R$$

$$(b) \quad \langle P \rangle = k_B T \left(\frac{\partial}{\partial V} \ln Q \right)_{T, N}$$

$$\ln Q = N \ln(V-b) - \ln N! + \frac{3N}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{3N}{2} \ln T$$

V is only in first term

$$\langle P \rangle = k_B T \left. \frac{\partial}{\partial V} \left(N \ln(V-b) \right) \right|_{T, N}$$

$$\langle P \rangle = N k_B T \frac{\partial}{\partial V} \ln(V-b) = \frac{N k_B T}{(V-b)} = \frac{n R T}{(V-b)}$$

$$(c) \quad A = -k_B T \ln Q \quad (\text{Helmholtz Free energy})$$

use $q_{\text{TRANS}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$ only degree of freedom for He, Ne

$$A = -k_B T \ln q_{\text{TRANS}} = -k_B T \left[\frac{3}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \ln V \right]$$

$\Rightarrow A \propto \ln(m)$ all other things being equal.

A for Ne $>$ A for He

$$(d) \quad q_{\text{elec}} = g_1 + g_2 e^{-\beta \epsilon_2} + g_3 e^{-\beta \epsilon_3} \dots$$

$$\beta = \frac{1}{k_B T} \quad \text{as } T \rightarrow 0 \quad \beta \rightarrow \infty$$

Thus all higher terms $e^{-\beta \epsilon}$ go to zero as $T \rightarrow 0$

$$q_{\text{elec}}(T \rightarrow 0) = g_1$$

$N=4$ atoms

$N=2$ atoms

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E)

NH_3
3 rotational
modes

vs HF

2 rotational
modes

$3N-3 = 9$ vibrational
modes

1 vibrational
mode

C_v of NH_3 should be much larger than that of HF

F)

Ignoring the mass difference the spring constant for the triple bond should be much larger than the spring constant for the double bond

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B} \quad , \quad \nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_{\text{eff}}}}$$

thus $\Theta_{\text{vib}} \propto \sqrt{\text{Spring Const}}$

G)

$I = 1^*$ has three states $m = +1, 0, -1$

$$q_{\text{magnetic}} = e^{+1 \gamma \mu_B} + e^{0 \gamma \mu_B} + e^{-1 \gamma \mu_B}$$

$$q_{\text{magnetic}} = 1 + e^{-\gamma \mu_B} + e^{+\gamma \mu_B}$$