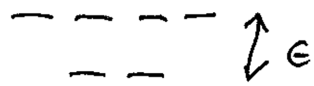
1) a) $q = 2 + 4e^{-\beta\epsilon}$



b) $Q = (2 + 4e^{-\beta\epsilon})^N$

c) $T \to 0,\ \beta \to \infty \quad q = 2$

$T \to \infty,\ \beta \to 0 \quad q = 6$

d) $U = -\frac{\partial}{\partial\beta} \ln (2 + 4e^{-\beta\epsilon})^N$

$$= \frac{+N\, 4\epsilon\, e^{-\beta\epsilon}}{2 + 4e^{-\beta\epsilon}} = \frac{N 4 \epsilon}{2e^{+\beta\epsilon} + 4}$$

e) $T = \frac{\epsilon}{k} \Rightarrow \epsilon = kT = \frac{1}{\beta}$

$$p_1 = \frac{4e^{-\beta\epsilon}}{2 + 4e^{-\beta\epsilon}}$$

@ $\epsilon = \frac{1}{\beta}$

$$p_1 = \frac{4e^{-1}}{2 + 4e^{-1}} = \frac{4}{2e + 4} = 0.424$$

2) $^{1}H^{35}Cl$ $\tilde{\nu} = 2991\ cm^{-1}$ $B = 10.6\ cm^{-1}$

a) $\Theta_R = \dfrac{hcB}{k} = \dfrac{(6.626\times10^{-34}\ J\cdot s)(3.0\times10^{10}\ \frac{cm}{s})(10.6\ cm^{-1})}{1.38\times10^{-23}\ J/K}$

$= 15.3\ K$

b) $\Theta_V = \dfrac{hc\tilde{\nu}}{k} = \dfrac{(6.626\times10^{-34}\ J\cdot s)(3.0\times10^{10}\ \frac{cm}{s})(2991\ cm^{-1})}{1.38\times10^{-23}\ J/K}$

$= 4308\ K$

c) @ 1000K high temp q is fine for rotation but <u>not</u> for vibration.

d) $$Q = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\ \frac{1}{\beta hcB}\ \frac{1}{1-e^{-\beta hc\tilde{\nu}}}\right)^N$$

e) $$q_v = \sum_{n=0}^{\infty} e^{-\beta nhc\tilde{\nu}} = \frac{1}{1-e^{-\beta hc\tilde{\nu}}}$$

$$p_1 = \frac{e^{-\beta hc\tilde{\nu}}}{\frac{1}{1-e^{-\beta hc\tilde{\nu}}}} = (1-e^{-\beta hc\tilde{\nu}})e^{-\beta hc\tilde{\nu}}$$

$$e^{-\frac{hc\tilde{\nu}}{kT}} = e^{-\frac{(6.626\times10^{-34})(3.0\times10^{10})(2991)}{(1.38\times10^{-23})(1000)}}$$

$= 0.013$

$p_1 = (1-0.013)(0.013) = 0.013$

3) a) $q = 1 + e^{-\beta\epsilon}$

$\epsilon = 3.65 \times 10^{-20}$ J

$\Delta\epsilon = 22$ kJ/mol

molecular

$\epsilon = \frac{22 \times 10^3 \text{ J/mol}}{6.023 \times 10^{23} \text{ mol}^{-1}}$

$= 3.65 \times 10^{-20}$ J

b) $Q = (1 + e^{-\beta\epsilon})^N$

c) $p(\text{boat}) = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}$

$= \frac{1}{e^{\beta\epsilon} + 1}$

d) @ 400 K

$[\text{boat}] = 1.0 \frac{\text{mol}}{\text{L}} \times \frac{1}{e^{\frac{3.65 \times 10^{-20}}{1.38 \times 10^{-23} \times 400}} + 1}$

$= 0.0013 \frac{\text{mol}}{\text{L}} = 1.3$ mmol/L

e) $U_c = -\frac{\partial}{\partial\beta} \ln(1 + e^{-\beta\epsilon})^N = \frac{N\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{N\epsilon}{e^{\beta\epsilon} + 1}$

$= \frac{6.02 \times 10^{23} \times 3.65 \times 10^{-20}}{e^{\frac{3.65 \times 10^{-20}}{1.38 \times 10^{-23} \times 400}} + 1} = 29.3$ J/mol

f) non-linear $\therefore$ $U_R = \frac{3}{2} nRT$

for 1.0 mol

$U = \frac{3}{2} RT + \frac{3}{2} RT + 29.3$

$= 3 \times 8.3 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 400\text{K} + 29.3$ J/mol

$= 9989 \frac{\text{J}}{\text{mol}} = 9.989$ kJ

4) a) $Q = \left(e^{+\frac{\beta\mu B}{2}} + e^{-\frac{\beta\mu B}{2}}\right)^N$ —— $+\frac{1}{2}\mu B$

—— $-\frac{1}{2}\mu B$

b) $U_s = -N \frac{\partial \ln}{\partial \beta}\left(e^{\frac{\beta\mu B}{2}} + e^{-\frac{\beta\mu B}{2}}\right)$

$$= \frac{-N\left(\frac{\mu B}{2} e^{+\frac{\beta\mu B}{2}} - \frac{\mu B}{2} e^{-\frac{\beta\mu B}{2}}\right)}{e^{\frac{\beta\mu B}{2}} + e^{-\frac{\beta\mu B}{2}}}$$

$$= \frac{-N\mu B}{2} \frac{e^{\frac{\beta\mu B}{2}} - e^{-\frac{\beta\mu B}{2}}}{e^{\frac{\beta\mu B}{2}} + e^{-\frac{\beta\mu B}{2}}}$$

c) $B \to 0$ $\quad U_s = -\frac{N\mu}{2} \cdot 0 \cdot \frac{1-1}{2} = 0$

levels have the same energy value

∴ cannot take up energy

d) $T \to \infty, \beta \to 0$ $\quad e^{\frac{\beta\mu B}{2}} \approx 1 + \frac{\beta\mu B}{2}$, $e^{-\frac{\beta\mu B}{2}} \approx 1 - \frac{\beta\mu B}{2}$

$$U_s = -\frac{N\mu B}{2} \frac{\left(1 + \frac{\beta\mu B}{2}\right) - \left(1 - \frac{\beta\mu B}{2}\right)}{2}$$

$$= \frac{-N\mu B}{2} \frac{\beta\mu B}{2} = -N\beta\frac{(\mu B)^2}{4} = \frac{-N(\mu B)^2}{4kT}$$

e) B^2 quadratic