Problem Set 4
CHEM 60641

1. $O_2 \rightleftharpoons 2O$

$$K_p(T) = \frac{P_O^2}{P_{O_2}} = k_B T \frac{(q_O/V)^2}{(q_{O_2}/V)}$$

$$\frac{q_O(T,V)}{V} = \left(\frac{2\pi m_O k_B T}{h^2}\right)^{3/2} g_O(0)\, e^{-D_e^O/k_BT}$$

De fined to be 0!

$$= \left(\frac{2\pi m_O k_B T}{h^2}\right)^{3/2} \times 9 \times 1$$

$$\frac{q_{O_2}(T,V)}{V} = \left(\frac{2\pi m_{O_2} k_B T}{h^2}\right)^{3/2} \times \frac{T}{2\theta_{rot}^{O_2}} \times \frac{e^{-\theta_{vib}^{O_2}/2T}}{1-e^{-\theta_{vib}^{O_2}/T}} \times g_0(O_2)\, e^{+D_e^{O_2}/k_BT}$$

electronic dissoc. energy

ground state dissoc. energy

$$= \left(\frac{2\pi m_{O_2} k_B T}{h^2}\right)^{3/2} \frac{T}{2\theta_{rot}^{O_2}} \left(1-e^{-\theta_{vib}/T}\right)^{-1} \times 3\; e^{+D_0^{O_2}/k_BT}$$

$\therefore$

$$\frac{q_{O_2}(T,V)}{V} = \left(\frac{2\pi \times 32 \times 1.661\times10^{-27}\,\frac{kg}{amu} \times 1.381\times10^{-23}\,\frac{J}{K} \times 3000K}{(6.626\times10^{-34}\,J\cdot s)^2}\right)^{3/2} \left(\frac{3000K}{2\times 2.07K}\right)\left(1-e^{-2256/3000}\right)^{-1} 3$$

$$\times\, e^{+118\,\frac{kcal}{mol}\times1000 / (1.9858\,\frac{cal}{mol\,K}\times 3000K)}$$

$$= 5.5945\times10^{33}\,\frac{1}{m^3} \times 724.63 \times 1.89187 \times 3 \times \cancel{[illegible]}\; 4.00\times10^{8}$$

$$\frac{q_{O_2}}{V} = \cancel{[illegible]}\; 9.21\times10^{45}\,\frac{1}{m^3}$$

$$\frac{q_O}{V} = 9\left(\frac{2\pi\times16\times1.661\times10^{-27}\,\frac{kg}{amu}\times1.381\times10^{-23}\,\frac{J}{K}\times3000K}{(6.626\times10^{-34}\,J\cdot s)^2}\right)^{3/2}$$

$$\frac{q_O}{V} = 1.78\times10^{34}\,\frac{1}{m^3}$$

1 (continued)

$$K_p = k_B T \frac{(q_i/V)^2}{(q_{0c}/V)}$$

$$= 1.381 \times 10^{-23} \frac{J}{K} \times 3000\,K \times \frac{\left(1.78 \times 10^{34} \frac{1}{m^3}\right)^2}{9.21 \times 10^{45} \frac{1}{m^3}}$$

$$= 1426 \frac{J}{m^3} = 1426 \text{ Pa}$$

$$K_p = 0.01407 \text{ atm}$$

2. $A \rightleftarrows 2B$

$$Q = \frac{q_A^{N_A}\, q_B^{N_B}}{N_A!\; N_B!}$$ Constraint : $2N_A + N_B - \text{Const} = 0$

$A = -k_B T \ln Q$

$= -k_B T \left(N_A \ln q_A - \ln N_A! + N_B \ln q_B - \ln N_B! \right)$

Stirling Approx: $\ln N! \approx N \ln N - N$

$$A \approx -k_B T \left(N_A \ln q_A - N_A \ln N_A + N_A + N_B \ln q_B - N_B \ln N_B + N_B \right)$$

add constraint:

$$A' = -k_B T\left(N_A \ln q_A - N_A \ln N_A + N_A + N_B \ln q_B - N_B \ln N_B + N_B \right) + \alpha\left(2N_A + N_B - c\right)$$

Minimize:

$$\frac{dA'}{\partial N_A} = -k_B T\left(\ln q_A - \frac{N_A^*}{N_A} - \ln N_A^* + 1 \right) + 2\alpha = 0$$

$$\frac{dA'}{\partial N_B} = -k_B T\left(\ln q_B - \frac{N_B^*}{N_B^*} - \ln N_B^* + 1 \right) + \alpha = 0$$

$\therefore$

$$-k_B T\left(\ln q_A - \ln N_A^* \right) + 2\alpha = 0$$
$$-k_B T\left(\ln q_B - \ln N_B^* \right) + \alpha = 0$$

solve to eliminate α

$$-k_B T\left(\ln q_A - \ln N_A^* - 2 \ln q_B + 2 \ln N_B^* \right] = 0$$

$$\ln q_A - 2 \ln q_B = \ln N_A^* - 2 \ln N_B^*$$

$$\boxed{\frac{q_A}{q_B^2} = \frac{N_A^*}{(N_B^*)^2}}$$

QED!

3 $\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightleftharpoons NO$

$$K = \frac{q_{NO}/V}{\sqrt{q_{O_2}/V}\sqrt{q_{N_2}/V}}$$

$$= \frac{q_{trans}^{NO}/V}{\sqrt{\frac{q_{trans}^{O_2}}{V}\frac{q_{trans}^{N_2}}{V}}} \times \frac{q_{rot}^{NO}}{\sqrt{q_{rot}^{O_2}q_{rot}^{N_2}}} \times \frac{\left(1-e^{-\theta_{vib}^{O_2}/T}\right)^{1/2}\left(1-e^{-\theta_{vib}^{N_2}/T}\right)^{1/2}}{1-e^{-\theta_{vib}^{NO}/T}} \frac{g_0(NO)}{\sqrt{g_0(O_2)\,g_0(N_2)}} \times$$

$$\times\ e^{-\left(D_0^{NO}-\frac{1}{2}D_0^{N_2}-\frac{1}{2}D_0^{O_2}\right)/k_BT}$$

$$= \frac{m_{NO}^{3/2}}{\sqrt{m_{N_2}^{3/2}\ m_{O_2}^{3/2}}} \times \frac{2\sqrt{\theta_{rot}^{O_2}\theta_{rot}^{N_2}}}{\theta_{rot}^{NO}} \frac{\left(1-e^{-\theta_{vib}^{O_2}/T}\right)^{1/2}\left(1-e^{-\theta_{vib}^{N_2}/T}\right)^{1/2}}{1-e^{-\theta_{vib}^{NO}/T}} \frac{2}{\sqrt{3\times 1}}$$

$$e^{-\left(150-\frac{118}{2}-\frac{225.1}{2}\right)\text{kcal/mol}/k_BT}$$

$$= \frac{30^{3/2}}{\sqrt{28^{3/2}\ 32^{3/2}}} \times \frac{2\sqrt{2.07\times 2.88}}{2.45} \times \frac{2}{\sqrt{3\times 1}} \times e^{-21.5\frac{\text{kcal}}{\text{mol}}\times 1000\frac{\text{cal}}{\text{kcal}}/1.9858\,T}$$

$$\times \frac{\left(1-e^{-2256/T}\right)^{1/2}\left(1-e^{-3374/T}\right)^{1/2}}{1-e^{-2719/T}}$$

$$K = 1.0033 \times 1.9931 \times 1.155 \times e^{-10827\,K/T} \times \frac{\left(1-e^{-2256/T}\right)^{1/2}\left(1-e^{-3374/T}\right)^{1/2}}{1-e^{-2719/T}}$$

$$\boxed{K = 2.31 \times e^{-10827\,K/T} \times \frac{\left(1-e^{-2256/T}\right)^{1/2}\left(1-e^{-3374/T}\right)^{1/2}}{\left(1-e^{-2719/T}\right)}}$$

T:	(1500)	(2000)	(2500)	
K_p	1.68×10^{-3}	1.028×10^{-2}	3.04×10^{-2}	anharmonicity is missing!
K_p(expt)	2.4×10^{-3}	1.5×10^{-2}	4.5×10^{-2}	

4. $H_2 + D_2 \rightleftharpoons 2HD$

$$K_p = K_c = \frac{q_{HD}^2}{q_{H_2} q_{D_2}}$$

$$= \frac{\left(\frac{2\pi m_{HD} kT}{h^2}\right)^3}{\left(\frac{2\pi m_{H_2} kT}{h^2}\right)^{3/2}\left(\frac{2\pi m_{D_2} kT}{h^2}\right)^{3/2}} \frac{\left(\frac{T}{\Theta_{rot}^{HD}}\right)^2}{\frac{T}{2\Theta_{rot}^{H_2}} \frac{T}{2\Theta_{rot}^{D_2}}} \times \frac{\left(\frac{e^{-\Theta_v^{HD}/2T}}{1-e^{-\Theta_v^{HD}/T}}\right)^2}{\left(\frac{e^{-\Theta_v^{H_2}/2T}}{1-e^{-\Theta_v^{H_2}/T}}\right)\left(\frac{e^{-\Theta_v^{D_2}/2T}}{1-e^{-\Theta_v^{D_2}/T}}\right)} \frac{e^{2D_e/kT}}{e^{D_e/kT} e^{D_e/kT}}$$

$$= \frac{m_{HD}^3}{(m_{H_2} m_{D_2})^{3/2}} \frac{4\Theta_{rot}^{H_2}\Theta_{rot}^{D_2}}{\Theta_{rot}^{HD}} \cdot \frac{(1-e^{-\Theta_v^{H_2}/T})(1-e^{-\Theta_v^{D_2}/T})}{(1-e^{-\Theta_v^{HD}})^2} e^{-\left(2\Theta_v^{HD}-\Theta_v^{H_2}-\Theta_v^{D_2}\right)/2T}$$

Now, since $\Theta_{vib} = \frac{h\nu}{k} = \frac{h\sqrt{\frac{k}{\mu}}}{2\pi k_B}$

the ratio depends only on reduced masses:

$$\frac{\Theta_{vib}^{HD}}{\Theta_{vib}^{H_2}} = \frac{\frac{h\sqrt{\frac{k}{\mu^{HD}}}}{2\pi k_B}}{\frac{h\sqrt{\frac{k}{\mu^{H_2}}}}{2\pi k_B}} = \sqrt{\frac{\mu_{H_2}}{\mu_{HD}}} = \sqrt{\frac{\frac{1}{2}}{\frac{2}{3}}} = \sqrt{\frac{3}{4}}$$

Table 6.1 tells us $\Theta_{vib}^{H_2} = 6215K$, so $\boxed{\Theta_{vib}^{HD} = 5{,}382 K}$

Likewise

$$\Theta_{rot} = \frac{h^2}{8\pi^2 I k_B} \qquad \frac{\Theta_{rot}^{HD}}{\Theta_{rot}^{H_2}} = \frac{\frac{h^2}{8\pi^2 I_{HD} k_B}}{\frac{h^2}{8\pi^2 I_{H_2} k_B}} = \frac{I_{H_2}}{I_{HD}} = \frac{\mu_{H_2} r_e^2}{\mu_{HD} r_e^2} = \frac{\mu_{H_2}}{\mu_{HD}}$$

$$\frac{\Theta_{rot}^{HD}}{\Theta_{rot}^{H_2}} = \frac{\frac{1}{2}}{\frac{2}{3}} = \frac{3}{4} \Longrightarrow$$

Table 6.1:

$\Theta_{rot}^{H_2} = 85.3K$

$\Theta_{rot}^{HD} = 69.975K$

4 continued):

So:

$$K_p = \frac{3^3}{(2\times 4)^{3/2}} \; \frac{4(85.3k)(42.7k)}{(69.975k)^2} \times \underbrace{\frac{\left(1-e^{-6215/T}\right)\left(1-e^{-4394/T}\right)}{\left(1-e^{-5382/T}\right)^2}}_{\text{all approx} \simeq 1} \; e^{-(10764-6215-4394)/2T}$$

$$\simeq \left(\frac{9}{8}\right)^{3/2} 4(0.7458) \quad 1 \times e^{-(10746-6215-4394)/2T}$$

$$K_p \simeq 3.55 \times e^{-78.5k/T}$$

← so there are some numerical issues, but this is approximately what McQ has!

5. a) Argon is a <u>monatomic</u> gas (no vibrations or ~~r~~rotations), so an approximate Q might be Q_{trans}. By equipartition, the average energy should have a $\frac{1}{2}k_BT$ contribution from each "squared" degree of freedom in the Hamiltonian:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m_i} = \sum_{i=1}^{N} \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m_i} = 3N \text{ "squared" terms}$$

$\therefore$

$$\langle E \rangle = 3N \times \tfrac{1}{2}k_BT$$

$\therefore$

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = \frac{3N k_B}{2} = \frac{3}{2}R = 12.47 \text{ J K}^{-1}\text{mo}$$

The <u>rest</u> of the heat capacity is due to intermolecular interactions, which are non-ideal.

b) <u>Water</u> has 3 translations, 3 rotations, & 3 vibrations per molecule, so by equipartition

$$\langle E \rangle = 9N \times \tfrac{1}{2}k_BT$$

$$C_V = \frac{9Nk_B}{2} = 37.413 \text{ J K}^{-1}\text{mol}^{-1}$$ (only about half of the total for a liquid)

The take home message is that equipartition doesn't handle the <u>intermolecular</u> energy contributions!

6) $$\mathcal{H} = -H \sum_n \sigma_n - \frac{J}{2} \sum_{n,n'}^{NN} \sigma_n \sigma_{n'}$$

We did much of this in class. at $T=0$, the only populated state is the lowest energy state.

$J > 0$: aligned states dominate

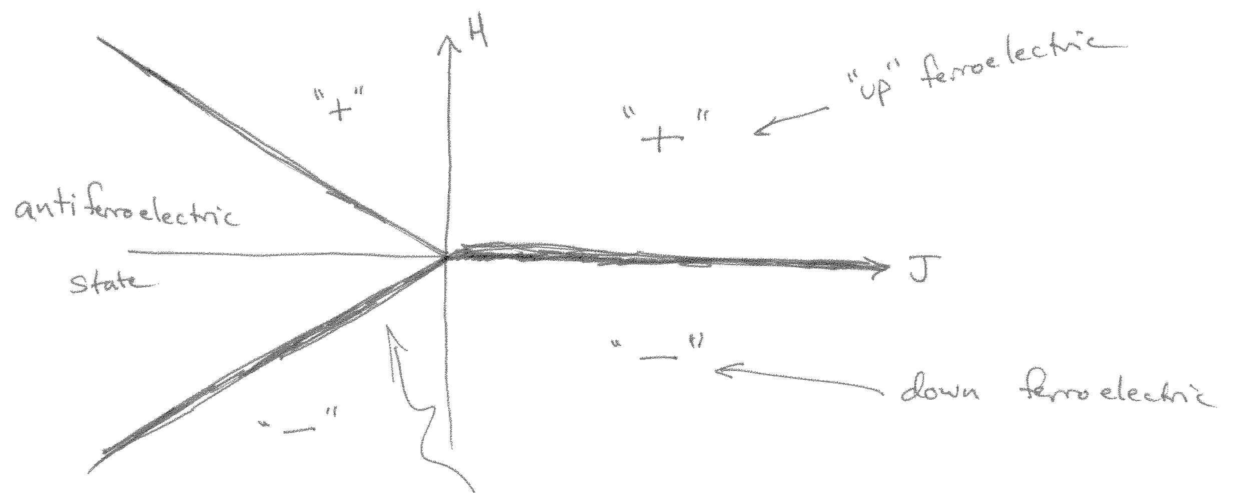
$H > 0$: spin up state dominates "+" state

$H < 0$: spin down state dominates "−" state

$J < 0$: anti-aligned states preferred
Now if H is large enough the "up" or "down" state could still be lower in energy:

$$\underbrace{-HN}_{\substack{\text{energy of} \\ N \text{ aligned} \\ \text{spins} \\ \text{(field contribution)}}} < \underbrace{-\frac{J}{2} N (2d)}_{\substack{\text{energy of} \\ N \text{ aligned} \\ \text{spins} \\ \text{(coupling contribution}}}$$

$H > Jd$ ← condition for H to dominate



Slope of coexistence line is dimensionality of system!

7) For two of these parts, we can use the zero field Q:

$$Q_N = (2\cosh\beta J)^N$$

$$\langle E\rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = \frac{-1}{(2\cosh\beta J)^N} N(2\cosh\beta J)^{N-1}(2\sinh\beta J)J$$

$$= -NJ\frac{2\sinh\beta J}{2\cosh\beta J} = -NJ\tanh\beta J = NJ\tanh\frac{J}{k_BT}$$

$$\boxed{\langle E\rangle = -NJ\tanh\frac{J}{k_BT}} \qquad \boxed{\frac{\langle E\rangle}{NJ} = -\tanh\frac{J}{k_BT}}$$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = -NJ\,\text{sech}^2\left(\frac{J}{k_BT}\right)\left(\frac{-J}{k_BT^2}\right)$$

$$\boxed{C_V = +\frac{J^2N}{k_BT^2}\text{sech}^2\frac{J}{k_BT}} \qquad \frac{C_V}{Nk_B} = +\frac{J^2}{k_B^2T^2}\text{sech}^2\left(\frac{J}{k_BT}\right) \Rightarrow \frac{C_V}{R} = +\left(\frac{J}{k_BT}\right)^2 \text{sec}$$

for the magnetic susceptibility, we need the partition function <u>with</u> the field turned on:

$$Q = e^{N\beta J}\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) - e^{-4\beta J}}\right]^N$$

$$\ln Q = N\beta J + N\ln\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H + e^{-4\beta J}}\right]$$

We did (in class) the derivation of the magnetization, $\langle m\rangle = \frac{\partial \ln Q}{\partial(\beta H)}$)

and got:

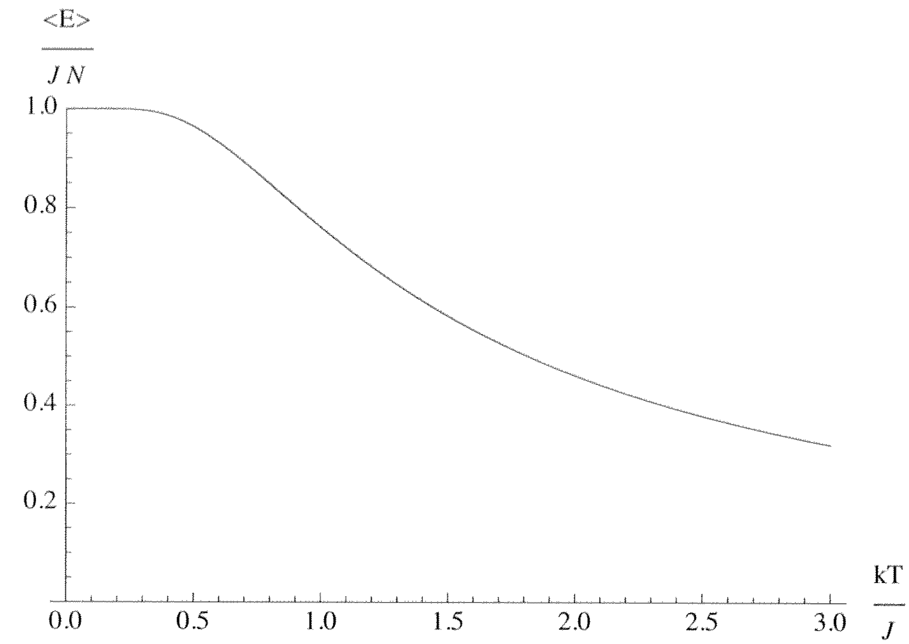
$$\langle m\rangle = \frac{\sinh(\beta H)}{(\sinh^2(\beta H) + e^{-4\beta J})^{1/2}}$$

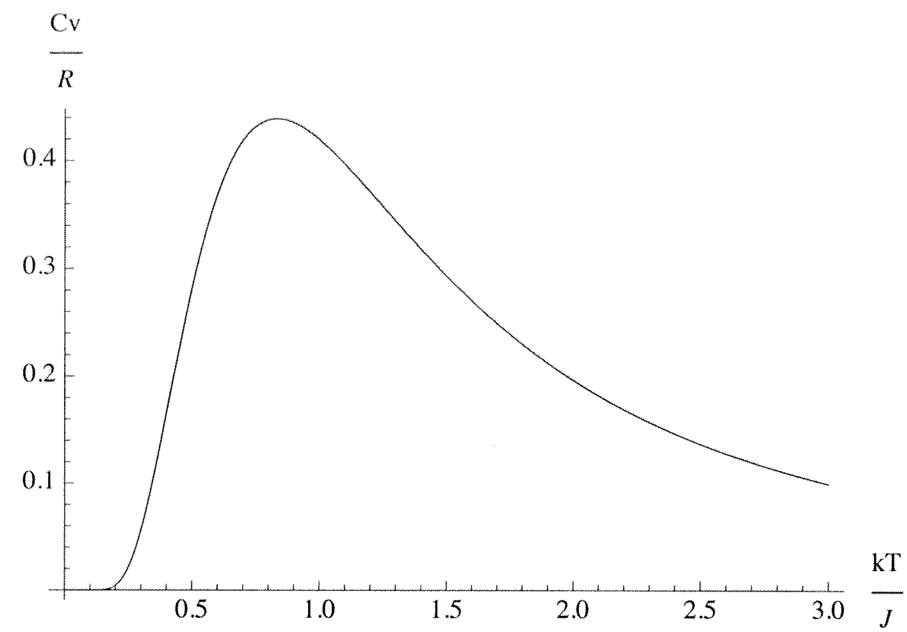
$$\chi = \lim_{H\to 0}\frac{\partial\langle m\rangle}{\partial H} = \frac{\beta\cosh(\beta H)}{\sqrt{\sinh^2(\beta H) + e^{-4\beta J}}} + \frac{-1}{2}\sinh(\beta H)\left(\sinh^2(\beta H) + e^{-4\beta J}\right)^{-3/2} 2\sinh(\beta H)\cosh(\beta H)$$

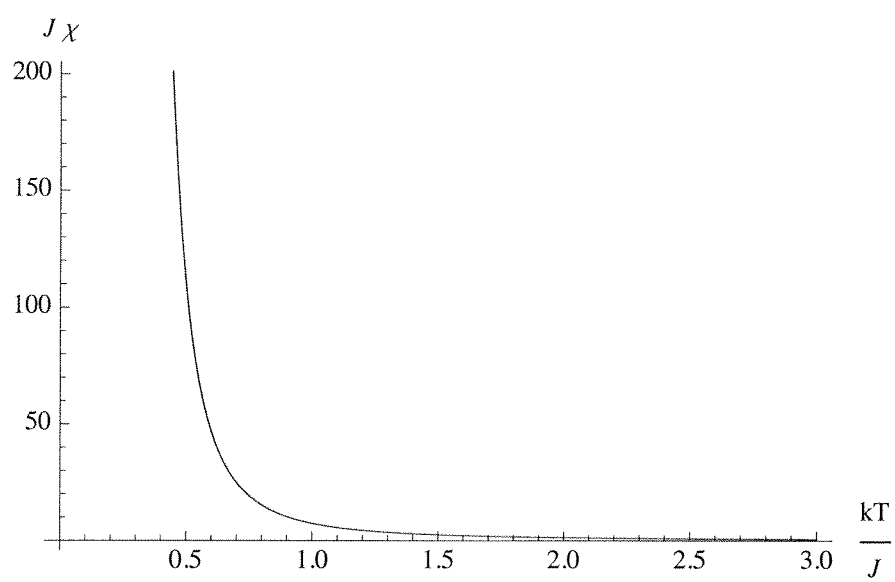
$$\left.\begin{aligned}\sinh(\beta H) &\to 0\\ \cosh(\beta H) &\to 1\end{aligned}\right\}\text{ as } H\to 0, \text{ so:}$$

$$\chi = \frac{\beta}{\sqrt{e^{-4\beta J}}} = \frac{\beta}{e^{-2\beta J}} = \frac{1}{k_BT}e^{2J/k_BT} \Rightarrow \chi J = \frac{J}{k_BT}e^{2J/k_BT}$$

plots follow:


<E>
J N
1.0
0.8
0.6
0.4
0.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
kT
J


Cv
R
0.4
0.3
0.2
0.1
0.5
1.0
1.5
2.0
2.5
3.0
kT
J


J χ
200
150
100
50
0.5
1.0
1.5
2.0
2.5
3.0
kT
J

8. $S = k \sum_i p_i \ln p_i$ $\qquad$ $\sum_i p_i = 1$

entropy $\qquad$ conservation of probability

There are 3 probabilities

p_a = probability of losing 1\$

p_b = probability of neutral outcome

p_c = probability of winning \$4

$$\langle \$ \rangle = (-1) p_a + (0) p_b + (4) p_c$$

$$\langle \$ \rangle = 4p_c - p_a \implies \boxed{4p_c - p_a - \langle \$ \rangle = 0}$$

$$\boxed{p_a + p_b + p_c = 1}$$

constraints

$$S = k(p_a \ln p_a + p_b \ln p_b + p_c \ln p_c)$$

$$F = k(p_a \ln p_a + p_b \ln p_b + p_c \ln p_c) + \alpha\left[4p_c - p_a - \langle \$ \rangle\right] + \beta\left[p_a + p_b + p_c - 1\right]$$

$$\frac{\partial F}{\partial \{p_a, p_b, p_c\}} = 0$$

$$\frac{\partial F}{\partial p_a} = k\left(\ln p_a + \frac{p_a}{p_a}\right) - \alpha + \beta) = 0 \qquad \ln p_a + 1 - \frac{\alpha}{k} + \frac{\beta}{k} = 0$$

$$\frac{\partial F}{\partial p_b} = k\left(\ln p_b + \frac{p_b}{p_b}\right) + \beta = 0 \qquad \ln p_b + 1 + \frac{\beta}{k} = 0$$

$$\frac{\partial F}{\partial p_c} = k\left(\ln p_c + \frac{p_c}{p_c}\right) + 4\alpha + \beta = 0 \qquad \ln p_c + 1 + \frac{4\alpha}{k} + \frac{\beta}{k} = 0$$

$$p_a = e^{-1} e^{\alpha/k} e^{-\beta/k}$$

$$p_b = e^{-1} e^{-\beta k}$$

$$p_c = e^{-1} e^{-4\alpha/k} e^{-\beta k}$$

general equations, now we appy constraints

8 continued)

$$P_a + P_b + P_c = 1$$

$$e^{-1} e^{\alpha/k} e^{-\beta/k} + e^{-1} e^{-\beta/k} + e^{-1} e^{-4\alpha/k} e^{-\beta/k} = 1$$

$$e^{-1} e^{-\beta/k} \left(e^{\alpha/k} + 1 + e^{-4\alpha/k} \right) = 1$$

$$e^{\alpha/k} + 1 + e^{-4\alpha/k} = e^{1} e^{\beta/k} \quad \text{or} \quad e^{-1} e^{-\beta/k} = \frac{1}{e^{\alpha/k} + 1 + e^{-4\alpha/k}}$$

$\therefore$

$$P_a = \frac{e^{\alpha/k}}{e^{\alpha/k} + 1 + e^{-4\alpha/k}}$$

$$P_b = \frac{1}{e^{\alpha/k} + 1 + e^{-4\alpha/k}}$$

$$P_c = \frac{e^{-4\alpha/k}}{e^{\alpha/k} + 1 + e^{-4\alpha/k}}$$

now probabilities are conserved.

Now:

$$4P_c - P_a = 0 \implies P_a = 4P_c$$

$$\frac{e^{\alpha/k}}{e^{\alpha/k} + 1 + e^{-4\alpha/k}} = \frac{4e^{-4\alpha/k}}{e^{\alpha/k} + 1 + e^{-4\alpha/k}}$$

$$e^{\alpha/k} = 4e^{-4\alpha/k}$$

$$\frac{\alpha}{k} = \ln 4 - \frac{4\alpha}{k} \implies \frac{5\alpha}{k} = \ln 4$$

$$\frac{\alpha}{k} = \frac{1}{5} \ln 4 = \ln\left[4^{(1/5)}\right]$$

$$\alpha/k = 0.277258872$$

$$P_a = \frac{e^{0.2772588\ldots}}{e^{0.27725} + 1 + e^{-1.109035489}} = \frac{1.3195079}{2.64938} = 0.49$$

$$P_b = \frac{1}{2.64938} = 0.377446$$

$$P_c = 1 - P_a - P_b = 0.13255$$

8 continued:

Therefore:

$$P_{lose\ \$1} = 0.49$$

$$P_{win\ \$1} = 0.377$$

$$P_{win\ \$4} = 0.1526$$

This will be neutral long-time averages for the casino!