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3.6 **(a)** **Assuming that the total number of microstates accessible to a given statistical system is Ω, show that the entropy of the system, as given by equation (3.3.13), is maximum when all Ω states are equally likely to occur.**

Starting with equation 3.3.13.

$$S = -k \sum_r P_r \ln P_r$$

Find when S is maximum.

$$\partial S = -k \partial \left(\sum_r P_r \ln P_r \right) \partial P_r \tag{1}$$

$$\partial S = -k \left(\sum_r \ln P_r + 1 \right) \partial P_r \tag{2}$$

Maximum entropy occurs when $\partial S = 0$.

$$-k \sum_r (\ln P_r + 1)\, \partial P_r = 0 \tag{3}$$

$$-\sum_r \ln P_r \partial P_r + \partial P_r = 0 \tag{4}$$

Use Lagrange's method of undetermined multipliers.

$$\sum_r P_r = 1 \tag{5}$$

$$\sum_r \partial P_r = 0 \tag{6}$$

$$\alpha \sum_r \partial P_r = 0 \tag{7}$$

Add equations (7) and (4).

$$\sum_r (\alpha - 1 - \ln P_r)\, \partial P_r = 0 \tag{8}$$

Since we're summing over all r, and α is independent of r, then the term inside the summation must be 0 for any r.

$$\alpha - 1 - \ln P_r = 0 \tag{9}$$

$$\ln P_r = \alpha - 1 \tag{10}$$

$$\boxed{P_r = e^{\alpha - 1}}$$

Since α is just a constant, we have just shown that for any r, P_r is a constant. Therefore, all P_r are equal thus indicating all Ω are equally likely.

(b) **If, on the other hand, we have an ensemble of systems sharing energy (with mean value E), then show that the entropy, as given by the same formal expression, is maximum when**

$P_r \propto \exp(-\beta E_r)$**,** β **being a constant to be determined by the given value of** E**.**
Since all systems are sharing energy, start with the following condition.

$$\sum_r P_r E_r = \bar{E} \tag{11}$$

$$\tag{12}$$

Use Lagrange's method of undetermined multipliers.

$$\sum_r E_r \partial P_r = 0 \tag{13}$$

$$\beta \sum_r E_r \partial P_r = 0 \tag{14}$$

Subtract step (14) from (8).

$$\sum_r (\alpha - 1 - \ln P_r - \beta E_r)\, \partial P_r = 0 \tag{15}$$

Since we're summing over all r and α is independent of r, then the term inside the summation must be 0 for any r.

$$\alpha - 1 - \ln P_r - \beta E_r = 0 \tag{16}$$

$$\ln P_r = \alpha - 1 - \beta E_r \tag{17}$$

$$P_r = \exp(\alpha - 1 - \beta E_r) \tag{18}$$

$$P_r = e^{\alpha-1} e^{-\beta E_r} \tag{19}$$

$$\tag{20}$$

$$\boxed{P_r \propto e^{-\beta E_r}}$$

3.8 Show that, for a classical ideal gas,

$$\frac{S}{Nk} = \ln\left(\frac{Q_1}{N}\right) + T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P$$

Find Q_1. We know that for an Ideal Gas:

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{21}$$

$$\frac{S}{Nk} = \ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + \frac{5}{2} \tag{22}$$

Also, we know

$$Q_N = \frac{1}{N!}\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right]^N \tag{23}$$

But, for indistinguishable particles:

$$Q_N = \frac{Q_1^N}{N!} \tag{24}$$

Set (23) and (24) equal to each other.

$$\frac{1}{N!}\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right]^N = \frac{Q_1^N}{N!} \tag{25}$$

$$\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right]^N = Q_1^N \tag{26}$$

$$Q_1 = \frac{V}{h^3}(2\pi mkT)^{3/2} \tag{27}$$

From Ideal Gas Law,

$$PV = NKT \tag{28}$$
$$V = \frac{1}{P}NKT \tag{29}$$

Use this result in (27).

$$Q_1 = \left(\frac{NKT}{P}\right)\frac{1}{h^3}\left(2\pi mkT\right)^{3/2} \tag{30}$$
$$Q_1 = \frac{NKT}{Ph^3}\left(2\pi mkT\right)^{3/2} \tag{31}$$

Find $\ln\frac{Q_1}{N}$.

$$\ln Q_1 = \ln\left[\frac{NKT}{Ph^3}\left(2\pi mkT\right)^{3/2}\right] \tag{32}$$
$$\ln Q_1 = \ln\left[\frac{NKT}{\left(\frac{NKT}{V}\right)h^3}\left(2\pi mkT\right)^{3/2}\right] \tag{33}$$
$$\ln Q_1 = \ln\left[\frac{VNKT}{NKTh^3}\left(2\pi mkT\right)^{3/2}\right] \tag{34}$$
$$\ln Q_1 = \ln\left[\frac{V}{h^3}\left(2\pi mkT\right)^{3/2}\right] \tag{35}$$
$$\ln\frac{Q_1}{N} = \ln\left[\frac{V}{Nh^3}\left(2\pi mkT\right)^{3/2}\right] \tag{36}$$

Find $\left(\frac{\partial \ln Q_1}{\partial T}\right)_P$.

$$\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\ln\left[\frac{NKT}{Ph^3}\left(2\pi mkT\right)^{3/2}\right]\right) \tag{37}$$
$$\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\ln\left[\frac{NK}{Ph^3}\left(2\pi mk\right)^{3/2}\right] + \ln\left[T^{5/2}\right]\right) \tag{38}$$
$$\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{\partial}{\partial T}\frac{5}{2}\ln T \tag{39}$$
$$\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{5}{2}\frac{1}{T} \tag{40}$$
$$T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P = \frac{5}{2} \tag{41}$$

Rewrite equation (22) but substituting (36) and (41).

$$\frac{S}{Nk} = \ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + \frac{5}{2} \tag{42}$$
$$\frac{S}{Nk} = \left(\ln\left[\frac{Q_1}{N}\right]\right) + \left(T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P\right) \tag{43}$$

$$\boxed{\frac{S}{Nk} = \ln\frac{Q_1}{N} + T\left(\frac{\partial \ln Q_1}{\partial T}\right)_P}$$

3.10 (a) The volume of a sample of helium gas is increased by withdrawing the piston of the containing cylinder. The final pressure P_f is found to be equal to the initial pressure P_i times $(Vi/Vf)^{1.2}$,

V_i and V_f being the initial and final volumes. Assuming that the product PV is always equal to $\frac{2}{3}U$, will (i) the energy and (ii) the entropy of the gas increase, remain constant, or decrease during the process?
(i). Energy
Compare the initial and final energies using the information given.

$$PV = \frac{2}{3}U \tag{44}$$
$$P_iV_i = \frac{2}{3}U_i \tag{45}$$
$$P_fV_f = \frac{2}{3}U_f \tag{46}$$
$$\frac{U_i}{U_f} = \frac{P_iV_i}{P_fV_f} \tag{47}$$

But we also know $P_f = P_i\left(V_i/V_f\right)^{1.2}$.

$$P_f = P_i\left(\frac{V_i}{V_f}\right)^{1.2} \tag{48}$$

Substitute (48) into (47).

$$\frac{U_i}{U_f} = \frac{P_iV_i}{P_i\left(\frac{V_i}{V_f}\right)^{1.2}V_f} \tag{49}$$
$$\frac{U_i}{U_f} = \frac{V_i}{V_f}\left(\frac{V_f}{V_i}\right)^{1.2} \tag{50}$$
$$\frac{U_i}{U_f} = \left(\frac{V_f}{V_i}\right)^{0.2} \tag{51}$$

Since $V_f > V_i$, we can see from (51) that $\frac{U_i}{U_f}$ must be greater than 1.

$$\frac{U_i}{U_f} > 1 \tag{52}$$

$$\boxed{U_f < U_i}$$

(ii). Entropy
For ideal gas, we know:

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{53}$$
$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mk\left(\frac{PV}{Nk}\right)}{h^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{54}$$
$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{2\pi mPV}{Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right] \tag{55}$$

Only P and V are changing. Find ΔS.

$$\Delta S = S_f - S_i \tag{56}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{N}\left(\frac{2\pi m P_f V_f}{Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right] - Nk\left[\ln\left(\frac{V_i}{N}\left(\frac{2\pi m P_i V_i}{Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right] \tag{57}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{N}\left(\frac{2\pi m P_f V_f}{Nh^2}\right)^{3/2}\right)+\frac{5}{2} - \ln\left(\frac{V_i}{N}\left(\frac{2\pi m P_i V_i}{Nh^2}\right)^{3/2}\right)-\frac{5}{2}\right] \tag{58}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{N}\left(\frac{2\pi m P_f V_f}{Nh^2}\right)^{3/2}\right) - \ln\left(\frac{V_i}{N}\left(\frac{2\pi m P_i V_i}{Nh^2}\right)^{3/2}\right)\right] \tag{59}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{V_i}\frac{N}{N}\left(\frac{2\pi m P_f V_f}{Nh^2}\right)^{3/2}\left(\frac{Nh^2}{2\pi m P_i V_i}\right)^{3/2}\right)\right] \tag{60}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{V_i}\left(\frac{2\pi m P_f V_f Nh^2}{2\pi m P_i V_i Nh^2}\right)^{3/2}\right)\right] \tag{61}$$

$$\Delta S = Nk\left[\ln\left(\frac{V_f}{V_i}\left(\frac{P_f V_f}{P_i V_i}\right)^{3/2}\right)\right] \tag{62}$$

$$\Delta S = Nk\left[\ln\left(\left(\frac{V_f}{V_i}\right)^{5/2}\left(\frac{P_f}{P_i}\right)^{3/2}\right)\right] \tag{63}$$

$$\Delta S = Nk\left[\ln\left(\left(\frac{V_f}{V_i}\right)^{5/2}\left(\left(\frac{V_i}{V_f}\right)^{1.2}\right)^{3/2}\right)\right] \tag{64}$$

$$\Delta S = Nk\left[\ln\left(\left(\frac{V_f}{V_i}\right)^{2.5}\left(\frac{V_i}{V_f}\right)^{1.8}\right)\right] \tag{65}$$

$$\Delta S = Nk\left[\ln\left(\left(\frac{V_f}{V_i}\right)^{0.7}\right)\right] \tag{66}$$

$$\frac{V_f}{V_i} > 1 \tag{67}$$

$$\tag{68}$$

$$\boxed{\Delta S > 0}$$

(b) If the process were reversible, how much work would be done and how much heat would be added in doubling the volume of the gas? Take $P_i = 1$ atm and $V_i = 1$ m^3 .
The change in pressure indicates that this process is an adiabatic process with $\gamma = 1.2$. To find the amount of work required for this process, use the equation for work for an adiabatic process.

$$W = P_i V_i^{\gamma}\frac{V_f^{1-\gamma} - V_i^{1-\gamma}}{1-\gamma} \tag{69}$$

$$P_i = 1 \text{ atm} \tag{70}$$

$$P_i = 101500 \text{ N m}^{-2} \tag{71}$$

$$V_i = 1 \text{ m}^3 \tag{72}$$

$$V_f = 2 \text{ m}^3 \tag{73}$$

$$W = (101500)\,(1)^{1.2}\,\frac{(2)^{1-1.2} - (1)^{1-1.2}}{1-1.2} \tag{74}$$

$$\boxed{W = 65.7 \text{ kJ}}$$

This process is adiabatic. Therefore, $Q = 0$ J.

$$\boxed{Q = 0 \text{ J}}$$

3.15 Show that the partition function $Q_N(V,T)$ of an extreme relativistic gas consisting of N monatomic molecules with energy–momentum relationship $\epsilon = pc$, c being the speed of light, is given by

$$Q_N(V,T) = \frac{1}{N!}\left[8\pi V\left(\frac{kT}{hc}\right)^3\right]^N$$

Study the thermodynamics of this system, checking in particular that

$$PV = \frac{1}{3}U$$
$$\frac{U}{N} = 3kT$$
$$\gamma = \frac{4}{3}$$

Next, using the inversion formula (3.4.7), derive an expression for the density of states $g(E)$ of this system.

Start with equation 3.5.5 from the textbook.

$$Q_N(V,T) = \frac{1}{N!h^{3N}}\int e^{-\beta H(q,p)}d\omega \tag{75}$$

Where the Hamiltonian for a photon, $H(q,p)$, is pc.

$$Q_N(V,T) = \frac{1}{N!h^{3N}}\int e^{-pc/kT}d\omega \tag{76}$$
$$Q_N(V,T) = \frac{1}{N!h^{3N}}\int e^{-c/kT\sum_i p_i}\Pi\left(d^3q_i d^3p_i\right) \tag{77}$$
$$Q_N(V,T) = \frac{V^N}{N!h^{3N}}\left[\int_0^\infty e^{-pc/kT}4\pi p^2 dp\right]^N \tag{78}$$
$$Q_N(V,T) = \frac{(4\pi V)^N}{N!h^{3N}}\left[\int_0^\infty e^{-pc/kT}p^2 dp\right]^N \tag{79}$$

Evaluate the integral by using the following definition.

$$\int_0^\infty x^n e^{-ax^b}dx = \frac{\Gamma\left(\frac{n+1}{b}\right)}{ba^{\frac{n+1}{b}}} \tag{80}$$
$$n = 2 \tag{81}$$
$$a = \frac{c}{kT} \tag{82}$$
$$b = 1 \tag{83}$$
$$\int_0^\infty e^{-pc/kT}p^2 dp = \frac{\Gamma(3)}{\left(\frac{c}{kT}\right)^3} \tag{84}$$
$$\int_0^\infty e^{-pc/kT}p^2 dp = \frac{(2)!}{\left(\frac{c}{kT}\right)^3} \tag{85}$$
$$\int_0^\infty e^{-pc/kT}p^2 dp = 2\left(\frac{kT}{c}\right)^3 \tag{86}$$

Use this result in equation (80).

$$Q_N(V,T) = \frac{(4\pi V)^N}{N!h^{3N}}\left[2\left(\frac{kT}{c}\right)^3\right]^N \tag{87}$$
$$Q_N(V,T) = \frac{1}{N!}\left(8\pi V\left(\frac{kT}{hc}\right)^3\right)^N \tag{88}$$

Use this result to find the Gibb's Free Energy.

$$A = -kT \ln Q_N \tag{89}$$

$$A = -kT \ln \left[\frac{1}{N!} \left(8\pi V \left(\frac{kT}{hc} \right)^3 \right)^N \right] \tag{90}$$

Use the Gibb's Free Energy to find thermodynamic quantities. Find P.

$$P = -\left(\frac{\partial A}{\partial V} \right)_{N,T} \tag{91}$$

$$P = -\frac{\partial}{\partial V} \left(-kT \ln \left[\frac{1}{N!} \left(8\pi V \left(\frac{kT}{hc} \right)^3 \right)^N \right] \right) \tag{92}$$

$$P = kT \frac{\partial}{\partial V} \left(\ln \frac{1}{N!} + 3N \ln \left[\frac{kT}{hc} \right] + N \ln [8\pi V] \right) \tag{93}$$

$$P = NkT \frac{1}{8\pi V} 8\pi \tag{94}$$

$$P = \frac{NkT}{V} \tag{95}$$

$$PV = NkT \tag{96}$$

Now, find free energy.

$$U = -\left(\frac{\partial A}{\partial \beta} \right) \tag{97}$$

$$U = -\frac{\partial}{\partial \beta} \left(\ln \frac{1}{N!} + 3N \ln \left[\frac{kT}{hc} \right] + N \ln [8\pi V] \right) \tag{98}$$

$$U = -\frac{\partial}{\partial \beta} \left(\ln \frac{1}{N!} + 3N \ln \left[\frac{1}{\beta hc} \right] + N \ln [8\pi V] \right) \tag{99}$$

$$U = -3N (\beta hc) \left(-\frac{1}{\beta^2 hc} \right) \tag{100}$$

$$U = 3N \frac{1}{\beta} \tag{101}$$

$$\frac{U}{N} = \frac{3}{\beta} \tag{102}$$

$$\frac{U}{N} = 3kT \tag{103}$$

$$\boxed{\frac{U}{N} = 3kT}$$

Use this result to solve for Pressure in terms of U. From before:

$$PV = NkT \tag{104}$$

$$PV = \left(\frac{U}{3kT} \right) kT \tag{105}$$

$$PV = \frac{U}{3} \tag{106}$$

$$\boxed{PV = \frac{U}{3}}$$

Now find the adiabatic index γ. Start by finding c_P.

$$c_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{107}$$

$$c_P = T\frac{\partial}{\partial T}k\left(\ln\frac{1}{N!} + 3N\ln\left[\frac{kT}{hc}\right] + N\ln\left[8\pi V\right]\right) \tag{108}$$

$$c_P = kT\frac{\partial}{\partial T}\left(3N\ln\left[\frac{kT}{hc}\right] + N\ln\left[\frac{8\pi NkT}{P}\right]\right) \tag{109}$$

$$c_P = 3NkT\frac{hc}{kT}\frac{k}{hc} + NkT\frac{P}{8\pi NkT}\frac{8\pi Nk}{P} \tag{110}$$

$$c_P = 3NkT\frac{1}{T} + NkT\frac{1}{T} \tag{111}$$

$$c_P = 3Nk + Nk \tag{112}$$

$$c_P = 4Nk \tag{113}$$

Now find c_V.

$$c_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} \tag{114}$$

$$c_V = \frac{\partial}{\partial T}\left(3NkT\right) \tag{115}$$

$$c_V = 3Nk \tag{116}$$

Use c_V and c_P to find γ.

$$\gamma = \frac{c_P}{c_V} \tag{117}$$

$$\gamma = \frac{4Nk}{3Nk} \tag{118}$$

$$\gamma = \frac{4}{3} \tag{119}$$

$$\boxed{\gamma = \frac{4}{3}}$$

Now find the equation of states. Start with equation 3.4.7.

$$g\left(E\right) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E}Q\left(\beta\right)d\beta \tag{120}$$

$$Q\left(\beta\right) = \frac{1}{N!}\left(8\pi V\frac{1}{\left(hc\right)^3}\right)^N\frac{1}{\beta^{3N}} \tag{121}$$

$$g\left(E\right) = \frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} e^{\beta E}\frac{1}{N!}\left(8\pi V\frac{1}{\left(hc\right)^3}\right)^N\frac{1}{\beta^{3N}}d\beta \tag{122}$$

$$g\left(E\right) = \left[\left(8\pi V\frac{1}{\left(hc\right)^3}\right)^N\frac{1}{N!}\right]\frac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty}\frac{e^{\beta E}}{\beta^{3N}}d\beta \tag{123}$$

$$\tag{124}$$

The right side of this equation (123) is the Laplace-transform of the function $\frac{x^n}{n!}$ for $x > 0$. Make this substitution.

$$g\left(E\right) = \left[\left(8\pi V\frac{1}{\left(hc\right)^3}\right)^N\frac{1}{N!}\right]\left(\frac{E^{3N-1}}{\left(3N-1\right)!}\right) \tag{125}$$

$$\boxed{g(E) = \left[\left(8\pi V \frac{1}{(hc)^3}\right)^N \frac{1}{N!}\right] \frac{E^{3N-1}}{(3N-1)!}}$$

3.20 Show that, for a statistical system in which the interparticle potential energy $u(r)$ is a homogeneous function (of degree n) of the particle coordinates, the virial V is given by

$$V = -3PV - nU$$

and, hence, the mean kinetic energy K by

$$K = -\frac{1}{2}V = \frac{1}{2}(3PV + nU) = \frac{1}{(n+2)}(3PV + nE)$$

here, U denotes the mean potential energy of the system while E = K + U. Note that this result holds not only for a classical system but for a quantum-mechanical one as well.

Start with the definition of the virial V.

$$V = \sum_i q_i F_i \tag{126}$$

$$V = \sum_{\text{ext}} q_i F_i + \sum_{\text{int}} q_i F_i \tag{127}$$

From equation 3.7.12, we know that $\sum_{\text{ext}} q_i F_i$ is $-3NkT$ or $-3PV$.

$$V = -3PV + \sum_{\text{int}} q_i F_i \tag{128}$$

We know that the internal potential U is some power of r.

$$U = \alpha r^n \tag{129}$$

$$F_i = -\frac{\partial U}{\partial r} \tag{130}$$

$$F_i = -\frac{\partial}{\partial r}(\alpha r^n) \tag{131}$$

$$F_i = -\alpha n r^{n-1} \tag{132}$$

Use this result in equation (128).

$$V = -3PV + \sum_{\text{int}} q_i \left(\alpha n r^{n-1}\right) \tag{133}$$

$$V = -3PV - \sum_{\text{int}} q_i \alpha n r^{n-1} \tag{134}$$

From section 7 in the book, q_i is analogous to r.

$$V = -3PV - r\alpha n r^{n-1} \tag{135}$$

$$V = -3PV - \alpha n r^n \tag{136}$$

$$V = -3PV - n(\alpha r^n) \tag{137}$$

$$V = -3PV - nU \tag{138}$$

$$\boxed{V = -3PV - nU}$$

We know that in the virial theorem, $K = -\frac{1}{2}\langle V \rangle$.

$$K = -\frac{1}{2}\langle V \rangle \tag{139}$$
$$E = K + U \tag{140}$$
$$U = E - K \tag{141}$$
$$K = -\frac{1}{2}\left(-3PV - nU\right) \tag{142}$$
$$K = -\frac{1}{2}\left(-3PV - nE + nK\right) \tag{143}$$
$$K = \frac{3}{2}PV + \frac{n}{2}E - \frac{n}{2}K \tag{144}$$
$$K + \frac{n}{2} = \frac{3}{2}PV + \frac{n}{2}E \tag{145}$$
$$K\left(1 + \frac{n}{2}\right) = \frac{3}{2}PV + \frac{n}{2}E \tag{146}$$
$$K\left(2 + n\right) = 3PV + nE \tag{147}$$
$$K = \frac{1}{2+n}\left(3PV + nE\right) \tag{148}$$

$$\boxed{K = \frac{1}{2+n}\left(3PV + nE\right)}$$