

PHYSICS 313

Thermodynamics

Solutions to problems

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Course web site: <http://www.physics.ubc.ca/~birger/313.toc/index.html>

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2003 Problems

Problem set 1 2003, Solution

Problem 1: The total internal energy is unchanged. Since the final temperature is the same on both sides the final temperature must be equal to the initial temperature. The pressure is also the same on both sides. Combining the two sides into a single system gives for the final pressure

$$P = \frac{nRT_0}{4V_0}$$

we also have

$$n = n_1 + n_2$$

$$n_1 = \frac{P_0 V_0}{RT_0}$$

$$n_2 = \frac{6P_0 V_0}{RT_0}$$

giving

$$n = 7 \frac{P_0 V_0}{RT_0}$$

The final pressure is then

$$P = \frac{7}{4} P_0$$

and

$$V_1 = \frac{4}{7} V_0$$

$$V_2 = \frac{24}{7} V_0$$

Problem 2:

a: The final volume is

$$V_f = V_i \left(\frac{P_i}{P_f} \right)^{1/\gamma} = 5.18 \text{ l}$$

b: The final temperature is

$$T_f = T_i \frac{P_f V_f}{P_i V_i} = 155.4 \text{ K}$$

Problem 3: For the pressure to double, the number of mols on the side where the temperature is constant must also double. This means that all the molecules must move over to that side. This requires the temperature on the hot side to be infinite which is not practical. In the general case the pressure is constant

$$n_c RT_c = n_h RT_h$$

With $n = n_c + n_h$ we find

$$n_c = \frac{T_h n}{T_h + T_c}$$

giving for the final pressure

$$P_f = \frac{n_c RT_c}{V} = 2P_i \frac{T_h}{T_c + T_h}$$

which agrees with the previous result that the pressure can only double in the limit $T_h \Rightarrow \infty$.

Problem set 2 2003, Solution

Problem 1:

$$p(N_H) = \left(\frac{1}{2}\right)^H \frac{N!}{N_H!(N - N_H)!}$$

a: Evaluating the exact expression we find

$$p(10) = .1762$$

b: Substituting the crude version of Stirling's formula

$$\ln n! = n \ln n - n$$

we find

$$p(10) = 1$$

which clearly isn't a very good approximation

c: Using

$$n! = n^n e^{-n} \sqrt{2\pi n}$$

I find

$$p(10) \approx \frac{1}{\sqrt{2\pi} 10} = .1784$$

which is a quite good approximation.

Problem 2:

the entropy of a mol with q quanta/oscillator is

$$S = 3N_A k_B (\ln(q+1) - \ln(q)) = 3R(\ln(q+1) - \ln(q))$$

where N_A is Avogadro's number and R is the gas constant. We find

$$S(q = 0.5) = 23.8 \text{ J K}^{-1} \quad S(q = 1) = 34.6 \text{ J K}^{-1} \quad S(q = 3) = 56.1 \text{ J K}^{-1}$$

Problem 3:

The internal energy is

$$U = \frac{3RnT_E}{\exp(T_E/T) - 1}$$

where n is the number of mols. With $T_E = 100 \text{ K}$ the energy per mol is thus

$$U(50) = 2.16 \cdot 10^{-22} \text{ J/oscillator}$$

$$U(100) = 8.04 \cdot 10^{-22} \text{ J/oscillator}$$

$$U(200) = 2.13 \cdot 10^{-21} \text{ J/oscillator}$$

Problem set 3 2003, solution

Problem 1:

a: The mass of an argon molecule is

$$m = \frac{39.95 \times 10^{-3}}{6.022 \times 10^{23}} = .6634 \times 10^{-25} \text{ kg}$$

giving for the thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = .1594665073 \times 10^{-10} \text{ m}$$

and for the entropy

$$S = R(\ln(\frac{k_B T}{P \lambda^3}) + \frac{5}{2})$$

with $P = 10^5 \text{ Nm}^{-2}$ we find

$$S = 154.99 \text{ JK}^{-1}$$

b: The change in entropy is

$$\Delta S = \int_i^f \frac{C_P dT}{T} = \frac{5R}{2} \ln \frac{600}{300} = 14.41 \text{ JK}^{-1}$$

c: The entropy doesn't change.

Problem 2:

a: The entropy associated with the outcome $m = 0$ after N tosses is

$$S = k_B \ln \left(\frac{2^N}{\sqrt{2\pi N}} \right) = 0.693 \times 10^6 k_B$$

b: The entropy in the two cases for the outcome $m = 100$ is

$$S(m = 100) = k_B \ln \left(\frac{2^N}{\sqrt{2\pi N}} \exp \left(-\frac{100^2}{2N} \right) \right) = S(m = 0) - 0.005 k_B$$

(almost undistinguishable from previous result)

Problem 3:

1 kg of aluminum contains 37.04 mol, so the specific heat is

$$C_{Al} = 3 \times 37.04 R = 924 \text{ JK}^{-1}$$

The specific heat of the water is $C_W = 1 \text{ kCal K}^{-1} = 4186 \text{ JK}^{-1}$

a: The final temperature can be obtained by solving

$$(400 - T)C_{AL} = (T - 300)C_W$$

or $T = 318 \text{ K}$.

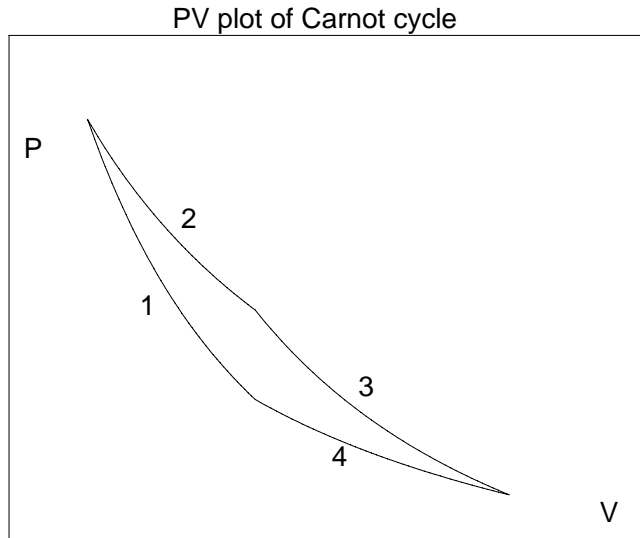
b: The change in entropy of the water is

$$\Delta S_W = C_W \ln \frac{318}{300} = 243.91 \text{ JK}^{-1}$$

c: The change in entropy of the aluminium is

$$\Delta S_{Al} = C_{Al} \ln \frac{318}{400} = -211.95 \text{ JK}^{-1}$$

so there is a net entropy gain in accordance with the second law.



Problem set 4 2003

Problem 1:

a: Consider the PV -plot of a Carnot cycle in figure

The corresponding ST -plot would be:

b: For the Otto cycle plotted in a PV -diagram the corresponding ST plot would be

Problem 2:

a: The Sackur-Tetrode formula for a monatomic ideal gas is

$$S = Nk_B \left(\ln\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2} \right)$$

giving with

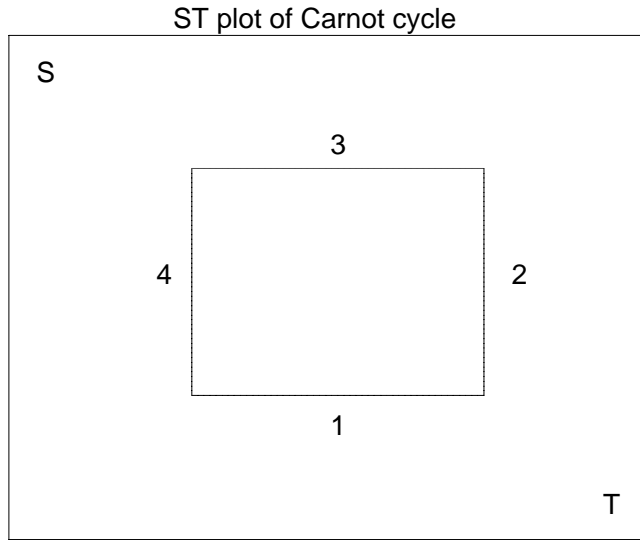
$$U = \frac{3Nk_B T}{2}$$

for the Helmholtz free energy

$$F = U - TS = -Nk_B T \left(\ln\left(\frac{V}{N\lambda^3}\right) + 1 \right)$$

b: The chemical potential is given by

$$\mu = \frac{G}{N} = \frac{F + PV}{N} = -k_B T \ln\left(\frac{k_B T}{P\lambda^3}\right)$$



The mass of an argon molecule is

$$m = \frac{39.95 \times 10^{-3}}{6.022 \times 10^{23}} = 0.6634 \times 10^{-25} \text{ kg}$$

giving for the thermal wavelength for Argon at 300 K and pressure 1 bar:

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = 0.1595 \times 10^{-10} \text{ m}$$

and for the chemical potential $\mu = 0.6685 \times 10^{-19} \text{ J}$.

c: The change in the chemical potential is

$$\Delta\mu = k_B T \ln \frac{P_f}{P_i} = 0.1917 \times 10^{-19} \text{ J}$$

assuming the temperature is unchanged.

Problem 3: From

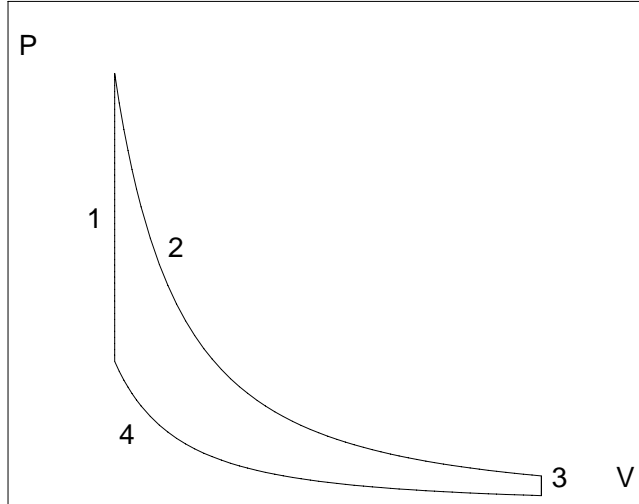
$$\frac{\partial G}{\partial P} = V = \frac{360 \times 10^3}{3 \times 10^8} = 1.2 \times 10^{-3}$$

we find for the density

$$\rho = \frac{m}{V} = 770 \text{ kg m}^{-3} = 0.77 \text{ kg liter}^{-1}$$

Oil?

PV plot of Otto cycle



Problem set 5 2003. Solution

Problem 1:

a: The Helmholtz free energy has the differential

$$dF = -SdT - PdV + \mu dN$$

Hence

$$\frac{\partial^2 F}{\partial V \partial T} = -\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_{V,N}$$

b: The Gibbs free energy has the differential

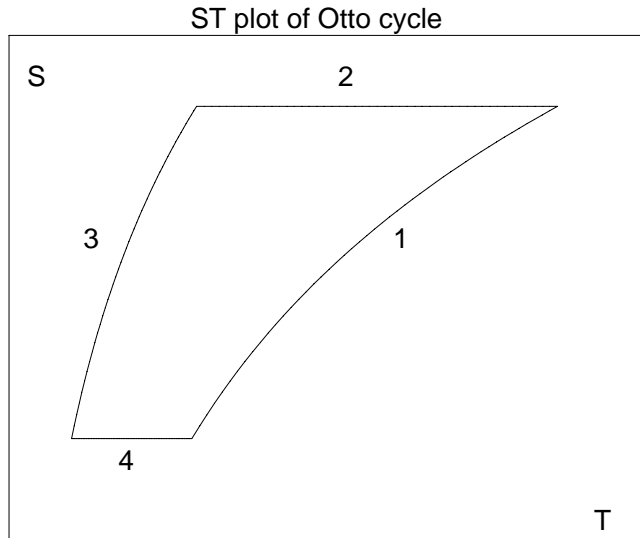
$$dG = -SdT + v dP + \mu dN$$

Hence

$$\frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_{T,N} = \frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial V}{\partial T}\right)_{P,N}$$

Problem 2:

When pepper is sprinkled on the water surface it will float on top. The reason it floats when sprinkled is the high surface tension of water. The pepper is actually heavier than water, as you can check by putting in the pepper first and then adding the water. In that case the pepper will stay at the bottom. When the water surface is touched by soap, with the pepper floating, the pepper flakes will rapidly be pushed to the side and some will



sink. The soap bar creates a soap film slick with reduced surface tension, pushing the pepper flakes to the side as the slick spreads.

Problem 3:

a: Substituting for the critical parameters I find

$$a = 0.1525 \times 10^{-47} \text{Nm}^{-4}; \quad b = 0.5055 \times 10^{-28} \text{m}^3$$

b: The $T = 37 \text{ K}$ isotherm were water a van der Waals fluid is drawn below for 1 mol of water

c: I find that the isotherm crosses 1 bar at 0.039 l while the volume of 1 mol of liquid water is 0.018. On the gas side the intercept is at 31 liter close to the ideal gas value.

Problem set 6 2003.Solution

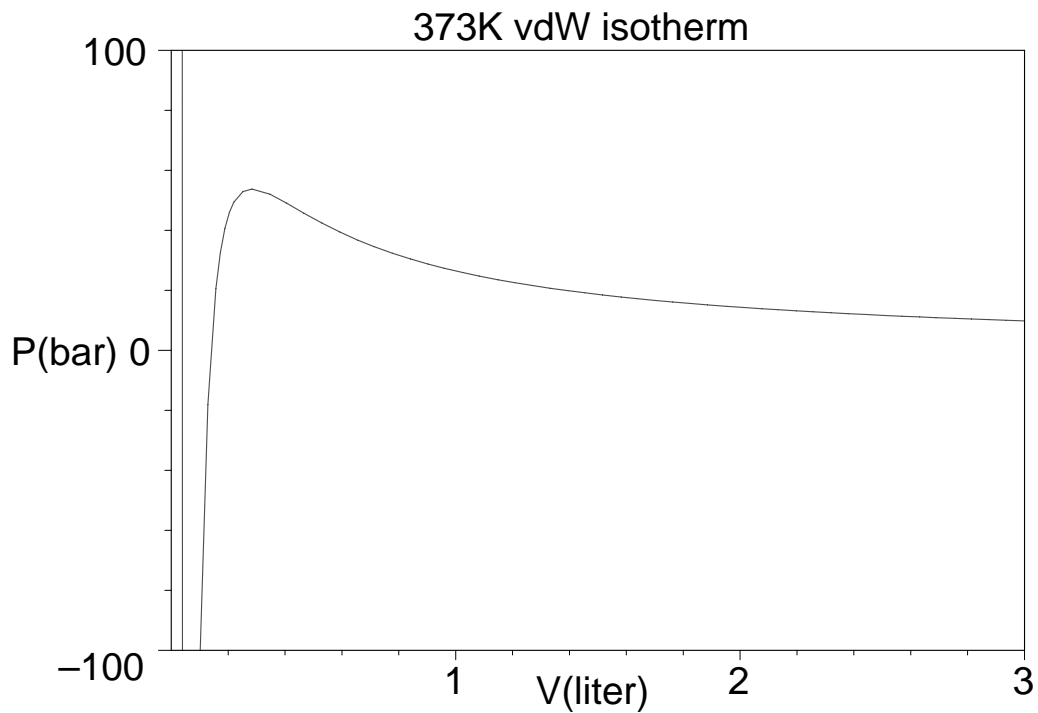
Problem 1:

The volume of 1 mol Na is $24 \times 10^{-6} \text{ m}^3$.

$$k_F = \left(\frac{N}{V 3\pi^2} \right)^{1/3} = 0.90 \times 10^{10} \text{m}^{-1}$$

The Fermi energy is thus

$$0.50 \times 10^{-18} \text{J} = 3.1 \text{eV}$$



Problem 2:

The Fermi wave vector is

$$k_F = \left(\frac{3\pi^2}{v} \right)^{1/3} = 0.86 \times 10^{10} \text{m}^{-3}$$

giving

$$T_F = \frac{\hbar^2 k_F^2}{2mk_b} = 6.0\text{K}$$

for the Fermi temperature and

$$v_F = \frac{\hbar k_F}{m} = 181 \text{ms}^{-1}$$

for the Fermi velocity.

Problem 3:

The probability that there are n links open is

$$p_n = \frac{e^{-n\beta\epsilon}}{Z}$$

$$Z = \sum_{n=0}^{\infty} e^{-n\beta\epsilon} = \frac{1}{1 - e^{-\beta\epsilon}}$$

The mean number of open link is

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} n e^{-n\beta\epsilon} = \frac{1}{e^{\beta\epsilon} - 1}$$

we have

$$\langle n^2 \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} n^2 e^{-n\beta\epsilon} = \frac{e^{\beta\epsilon} + 1}{(e^{\beta\epsilon} - 1)^2}$$

giving for the variance

$$\langle n^2 \rangle - \langle n \rangle^2 = \frac{e^{-\beta\epsilon}}{(1 - e^{-\beta\epsilon})^2}$$

Review problem set for 2003 final. Solution.

Problem 1:

The Helmholtz free energy is

$$F = -Nk_B T \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + 1 \right) - \frac{aN^2}{V}$$

$$v_q = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}$$

We find for the entropy

$$S = -\frac{\partial F}{\partial T} = Nk_B \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + 1 \right) - \frac{Nk_B T}{v_q} \frac{\partial v_q}{\partial T}$$

or

$$S = Nk_B \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + 1 \right) + \frac{3Nk_B}{2}$$

so that the internal energy is

$$U = \frac{3Nk_B T}{2} - \frac{aN^2}{2V}$$

b: When the gas is heated from temperature T to $2T$ at constant volume the work is

$$W = 0$$

and the heat is

$$Q = \Delta U = \frac{3Nk_B\Delta T}{2} = \frac{3Nk_BT}{2}$$

The pressure is

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}$$

When expanded from volume V to $2V$ at constant temperature the work is

$$W = - \int_V^{2V} P dv = -Nk_BT \ln \frac{2V - Nb}{V - Nb} + \frac{aN^2}{2V}$$

The change in internal energy is

$$\Delta U = \frac{aN^2}{V}$$

giving for the heat at the second stage

$$Q = \Delta U - W = Nk_BT \ln \frac{2V - Nb}{V - Nb}$$

Problem 2:

a: The ideal voltage of the cell at 298 K, 1 bar is

$$\frac{\Delta G_{process}}{2N_A e} = \frac{237.13}{2 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-19}} = 1.23 \text{ V}$$

b:

$$\frac{\partial G}{\partial T} = -S$$

The entropy change in the reaction is

$$\Delta S = S_i - S_f = 130.68 + \frac{205.146}{2} - 69.91 = 163.34 \text{ JK}^{-1}$$

The change from the result in **a:** is, if the temperature is raised to 350K and the pressure remains 1 bar

$$\Delta V \approx -\frac{T\Delta S}{2N_A e} = -0.044 \text{ V}$$

i.e. the voltage decreases by a small amount when the temperature is increased.

c:

$$\frac{\partial G}{\partial P} = V$$

The volume of the liquid is small compared to that of the gas so we neglect the change in G for the liquid water. We thus have for the change in Gibbs free energy per mol of gas

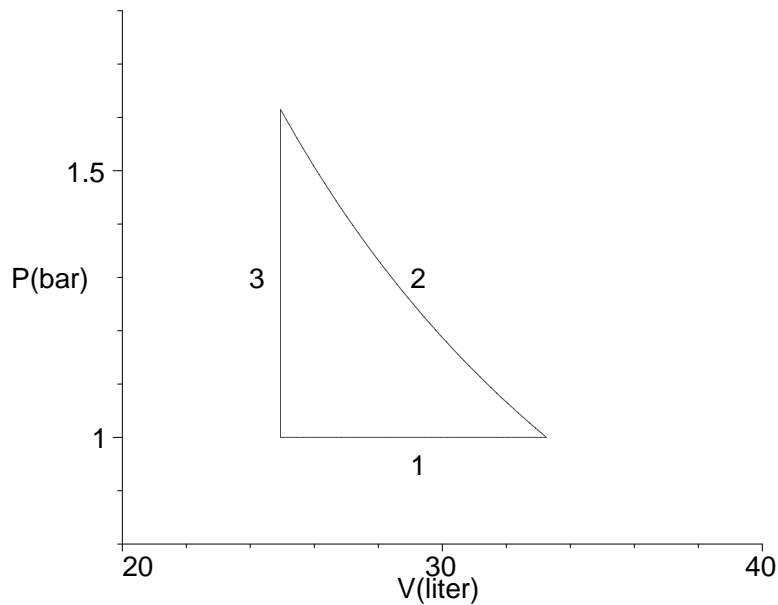
$$\int_{P_i}^{P_f} V dp = \int_{P_i}^{P_f} \frac{RT}{P} dp = RT \ln \frac{P_f}{P_i}$$

$$\Delta V = 1.5 \frac{RT \ln(20)}{2N_A e} = .06 V$$

The voltage *increases*.

Problem 3:

a:



b: The cycle is counterclockwise in the figure above \Rightarrow it therefore works as a *heat pump* or a *fridge*.

c: In the first step

$$V_1 = \frac{V_0 T_1}{T_0}$$

$$W = -P_0(V_1 - V_0) = -P_0 V_0 \frac{T_1 - T_0}{T_1} = -R(T_1 - T_0) = -835.5 \text{ J}$$

$$Q = C_P R(T_1 - T_0) = \frac{5}{2} 8.315 \times 100 = 2078.75 \text{ J}$$

In the second step

$$T_2 = T_1 \left(\frac{V_1}{V_0} \right)^{4/3} = T_1 \left(\frac{T_1}{T_0} \right)^{4/3}$$

$$W = U_2 - U_1 = C_V(T_2 - T_1) = \frac{3RT_1}{2} \left[\left(\frac{T_1}{T_0} \right)^{4/3} - 1 \right] = 1054.7 \text{ J}$$

$$Q = 0$$

In the third step

$$W = 0$$

$$Q = -C_V(T_2 - T_0) = \frac{3}{2} R \left[T_1 \left(\frac{T_1}{T_0} \right)^{4/3} - T_0 \right] = -2302 \text{ J}$$

Problem 4:

a: Let m be the mass of a molecule and M the mass of a mol. At constant temperature

$$P = P_0 \exp\left(-\frac{mgh}{k_B T}\right) = P_0 \exp\left(-\frac{Mgh}{RT}\right) = .558 \text{ bar}$$

b: The pressure satisfies the differential equation

$$dp = -\rho g dh$$

$$\rho = \frac{Nm}{V} = \frac{PM}{RT}$$

giving

$$\frac{dP}{P} = \frac{Mg}{R(T_0 - lh)} dh$$

$$\ln \frac{P}{P_0} = \frac{Mg}{Rl} \ln\left(1 - \frac{lh}{T_0}\right)$$

$$P = P_0 \exp\left(\frac{Mg}{Rl} \ln\left(1 - \frac{lh}{T_0}\right)\right) = .527 \text{ bar}$$

Problem 5:

a: The first part involves numerical work which is a bit more than can be expected at an exam. The entropy of an Einstein solid is

$$S = Nk_B \left(\left(1 + \frac{q}{N}\right) \ln \left(1 + \frac{q}{N}\right) - \frac{q}{N} \ln \left(\frac{q}{N}\right) \right) = 3N_A R \left(\left(1 + \frac{q}{N}\right) \ln \left(1 + \frac{q}{N}\right) - \frac{q}{N} \ln \left(\frac{q}{N}\right) \right)$$

where q is the number of vibrational quanta. Solving numerically for q/N with the given value of S gives

$$\frac{q}{N} = .682$$

solving numerically for T_E in

$$\frac{q}{N} = \frac{1}{\exp\left(\frac{T_E}{T}\right) - 1}$$

gives $T_E = 269$ K. **b:** The specific heat per mol is approximately

$$C = 3R = 25.0 \text{ J K}^{-1}$$

c: To find the Fermi energy we first find the Fermi wave vector

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} = \left(\frac{9\pi^2 M N_A}{\rho} \right)^{1/3} = .175 \times 10^{11} \text{ m}^{-3}$$

Here the number of conduction electrons in a mol N is $3N_a$ and ρ is the mass density and M the molecular weight The Fermi energy is thus

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = 0.187 \times 10^{-17} \text{ J} = 11.7 \text{ eV}$$

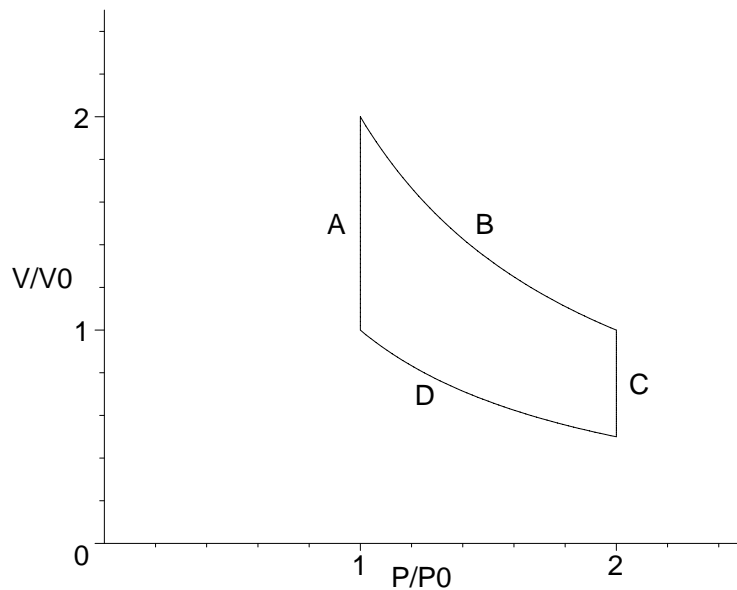
where m is the electron mass.

d: The Fermi velocity is

$$\frac{\hbar k_F}{m} = 2.0 \times 10^6 \text{ ms}^{-1}$$

e: The Fermi temperature is

$$T_F = \frac{\epsilon_F}{k_B} = 1.35 \times 10^5 \text{ K}$$



2003 Exams

Midterm October 1 2003. Solution.

a: A P, V diagram for the process looks like the figure below **b:** With the sign convention

$$\Delta U = Q + W$$

we have

$$Q_A > 0; W_A = 0; Q_B > 0; W_B < 0; Q_C < 0; W_C = 0; Q_D < 0; W_D > 0$$

c: The final Temperature after step **A** is $2T_0$. The number of moles is $\frac{P_0 V_0}{RT_0}$

$$Q_A = \frac{f P_0 V_0}{2}, W_A = 0$$

$RT = 2P_0 V_0$ in step **B** giving

$$Q_B = -W_B = 2P_0 V_0 \ln 2$$

$$Q_C = -\frac{f P_0 V_0}{2}, W_C = 0$$

$$Q_D = -W_D = -P_0 V_0 \ln 2$$

Problem 2:

a: The mass of the air inside the balloon is

$$\frac{MPV}{RT_{hot}} = 387.5 \text{ kg}$$

b: The mass of the cold air displaced by the balloon is

$$\frac{MPV}{RT_{cold}} = 581.3 \text{ kg}$$

The difference is the maximum payload 193.8 kg.

Problem 3:

a: The average number vibrational quanta per oscillator will be

$$\frac{q}{N} = \frac{1}{\exp(\frac{T_E}{T}) - 1} = .58$$

b: The entropy per oscillator is

$$S = -k_B \left(\frac{N+q}{N} \ln \frac{N+q}{N} + \frac{q}{N} \ln \frac{q}{N} \right) = 1.04 k_B$$

Midterm November 5 2003. Solution.

Problem 1: **a** From

$$S = Nk_B \left[\ln \left(\frac{V}{v_q N} \right) + \frac{5}{2} \right]$$

and the ideal gas law we find

$$v_q = \frac{k_B T}{P} \exp \left(-\frac{S}{Nk_B} + \frac{5}{2} \right)$$

Substituting $S = 154.84 \text{ J/K}$, we find $v_q = .410029 \times 10^{-32} \text{ m}^3$.

b: The entropy of 1 mol of Argon at 400 K is then (with $V_f = V_i T_f / T_i$ and $v_{qf} = v_{qi} (T_f / T_i)^{3/2}$)

$$S_f = S_i + \frac{R \times 5}{2} \ln \frac{400}{298} = 160.96 \text{ J/K}$$

Alternatively

$$\Delta S = C_P \int_{298}^{400} \frac{dT}{T} = \frac{5R}{2} \ln \frac{400}{298}$$

Problem 2:

a: The energy is unchanged so the Temperature is $T_f = 350$ K. The pressure is thus

$$P_f = \frac{RT_f}{V} = 29.1 \text{ bar}$$

b: The change in the entropy is

$$\Delta S = C_V \left(\int_{300}^{350} \frac{dT}{T} + \int_{400}^{350} \frac{dT}{T} \right) = \frac{3R}{2} \ln\left(\frac{350^2}{300 \times 400}\right) = .257 \text{ JK}^{-1}$$

c: Yes, C_V is different for a diatomic gas.

Problem 3:

a:

$$\Delta G = V\Delta P = 18 \times 10^{-6} \times 299. \times 10^5 = 538.2 \text{ J}$$

b:

$$\Delta G = \int_{P_i}^{P_f} V dP = 1.5RT \ln(300) = 21.2 \text{ kJ}$$

c: The minimum voltage required will increase since the Gibbs free energy of the gases produced will increase more than the free energy of the liquid consumed. Another way of looking at it is to note that the liberated gases will have to do more work against the environment. Hence more work is required and the voltage needs to be increased.

Sessional exam, December 10 2003. Solution

Problem 1: Given

$$F = -Nk_B T \left(\ln\left(\frac{V - Nb}{Nv_q}\right) + 1 \right) - \frac{aN^2}{V}$$

$$v_q = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}$$

a: The pressure is

$$P = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

b: The internal energy can be obtained by first computing

$$S = -\frac{\partial F}{\partial T}$$

and substituting into

$$U = F - TS$$

Alternatively, we can find the internal energy from

$$U = \frac{\partial \beta F}{\partial \beta}$$

We have

$$\beta F = N \left(\ln \left(\frac{V - Nb}{N \left(\frac{2\pi\hbar^2\beta}{mk_B} \right)^{3/2}} + 1 \right) - \frac{aN^2\beta}{V} \right)$$

differentiating we find

$$U = \frac{3N}{2\beta} - \frac{aN^2}{V^2} = \frac{3Nk_B T}{2} - \frac{aN^2}{V^2}$$

c: The specific heat C_V is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V,T} = \frac{3Nk_B}{2}$$

Problem 2:

a: From the table the available work available under ideal conditions is

$$\Delta G_f - \Delta G_i = 6\Delta G_{CO_2} + 6\Delta G_{H_2O} - \Delta G_{glucose} - 6\Delta G_{O_2} = -2878.94 kJ$$

Since work is positive if done on the system a negative ΔG means that the system (muscle) does the work.

b:

$$S_f - S_i = 6S_{CO_2} + 6S_{H_2O} - S_{glucose} - 6\Delta S_{O_2} = 259 \text{ JK}^{-1}$$

$$T\Delta S = 273 \times 259 = -77.20 \text{ kJ}$$

The negative sign in the entropy change means that the system gives up heat, in agreement with the everyday experience that you get hot when doing physical work.

Problem 3:

a: The probability per unit volume that a state with wave vector k is occupied at temperature T is

$$p_{\vec{k}} = \frac{e^{-\beta\hbar ck}}{Z}$$

where (with a factor 2 for spin)

$$Z = 1 + e^{-\beta\hbar ck}$$

b: The number of allowed wave-vectors between k and $k + dk$ is

$$\frac{4\pi k^2 dk}{(2\pi)^3}$$

The number of neutrinos expected in a volume V at temperature T is thus

$$\langle n \rangle = \frac{8V\pi}{(2\pi)^3} \int_0^\infty \frac{k^2 e^{-\beta \hbar k c} dk}{e^{-\beta \hbar c} + 1} = \frac{1.80 k_B^3 T^3}{\pi^2 \hbar^3 c^3}$$

c: Substituting

$$k_B = 1.381 \times 10^{-23} \text{ JK}^{-1}; \quad T = 1.95 \text{ K}; \quad \hbar = 0.10546 \times 10^{-33} \text{ Js}; \quad c = 2.998 \times 10^8 \text{ ms}^{-1}$$

gives

$$\langle n \rangle = 1.1 \times 10^8 \text{ m}^{-3}$$

Problem 4:

a: The volume of 1 kg of water is 0.001 m^3 , while the volume of 1 kg of ice is $1/0.917 = 0.001090 \text{ m}^3$. From the Clausius-Clapeyron equation

$$\Delta T = \frac{T \Delta V \Delta P}{L} = \frac{273 \times (0.001 - 0.001090) \times 99 \times 10^5}{3330000} = -0.72 \text{ K}$$

b:

$$L = \Delta H = \Delta U + \Delta(PV)$$

The first term on the right hand side represents the change in internal energy while the second represents the work done by the vapor against the atmospheric pressure. The volume of 1 mol water vapor is

$$V = \frac{RT}{P}$$

neglecting the volume of liquid water gives for the work term

$$W = RT = 3.10 \text{ KJ}$$

giving for the change in internal energy

$$U = L - W = 37.56 \text{ KJ}$$

Problem 5:

a: After the compression the partial pressure of the water vapor remains

1.013 bar. The air pressure is then $P_{af} = 2.987$ bar. The number of mols of air is equal to the initial number of mols of vapor.

$$n_i = \frac{PV}{RT} = \frac{10^5}{373 \times 8.315} = 32.34$$

The final volume is thus

$$V_f = \frac{n_i RT}{P_{af}} = 0.335 \text{ m}^3$$

What is the volume of gas at equilibrium under the new conditions?

b: The number of mols of vapor when the gas is compressed is

$$n_f = \frac{1.013 \times 10^5 \times 0.335}{8.315 \times 373} = 10.94$$

The number of mols of liquid water is thus

$$n_l = n_i - n_f = 21.4$$

The weight of the water is

$$21.4 \times 0.018 = 0.385 \text{ kg}$$

2002 Problems

Problem set 1 2002. Solution

Problem 1:

a:

Since $\Delta V \ll V$ we can put

$$\Delta V_{total} = \Delta V_1 + \Delta V_2 + \cdots = V * (\beta_1 \Delta T_1 + \beta_2 \Delta T_2 + \cdots)$$

Adding up the terms yields $\Delta V = 0.0425$ liter.

b:

The work is (with the sign convention used in class)

$$W = -P\Delta V = 10^5 \times 0.0425 \times 10^{-3} = -4.25\text{J}$$

c: C_P for water is $4.186 \text{ kJ kg}^{-1}\text{K}^{-1}$. We have

$$C_V = \left. \frac{\partial U}{\partial T} \right|_V$$

$$C_P = \frac{\partial U}{\partial T}|_P + P \frac{\partial V}{\partial T}|_P$$

Since we are only interested in an estimate we neglect the difference between the derivatives of U at constant P and V and find

$$C_V = C_P - P \frac{\Delta V}{\Delta T} = 4.186 \times 10^3 - 4.25/100$$

giving

$$\gamma = C_P/C_V = 1.00001$$

Problem 2:

The volume change for one degree is

$$\Delta V = \pi d^2/4 * \Delta h = \pi(0.25 \times 10^{-3})^2 \times 10^{-3}$$

The volume of the bulb is thus

$$\Delta V/\beta = 1.08 \times 10^{-6} \text{m}^3 = 1.08 \text{ml}$$

b: The bulk expansion coefficient is 3 times the linear coefficient, i.e. about 10% of the coefficient for mercury. So the error is about 10%. **c:** The volume of the column is

$$\frac{\pi h d^2}{4} = 2.0 \times 10^{-8} \text{m}^3$$

which is $\approx 1/50$ of the volume of the bulb. So the error here is small.

Problem 3:a

The number of mols in 1 kg

$$n = \frac{1000}{55.845} = 17.9$$

The heat capacity per kg is thus

$$C_I = 3nR = 447 \text{J kg}^{-1} \text{K}^{-1}$$

much less than for water!

b: The heat needed to boil the water is

$$Q = m(\Delta T_w C_{water} + L)$$

where m is the mass and L is the latent heat of evaporation. The amount of iron is then

$$\frac{Q}{C_I \Delta T_I} = \frac{10 \times 4180(80 + 540)}{447 \times 900} = 64.5 \text{kg!}$$

Problems set 2. Solution

Problem 1:

a: We have

$$\frac{dP}{P} = -\frac{mgdz}{kT_o}$$

with solution

$$\ln P = -\frac{mgz}{kT_o} + \text{const}$$

With the boundary condition at $z = 0$ we find

$$P = P_o \exp\left(\frac{-mgz}{kT}\right)$$

b:

The differential for the pressure now becomes

$$\frac{dP}{P} = -\frac{mgdz}{k(T_o - lz)}$$

Integrating it we get

$$\ln P = \text{const} + \frac{mg}{kl} \ln\left(1 - \frac{lz}{T_o}\right)$$

The boundary condition at $z = 0$ gives $\text{const} = -\ln P_o$ and the expressions can be rewritten as

$$P = P_o \exp\left(\frac{mg}{kl} \ln\left(1 - \frac{lz}{T_o}\right)\right)$$

Obviously this formula is only valid for heights

$$z < \frac{T_o}{l}$$

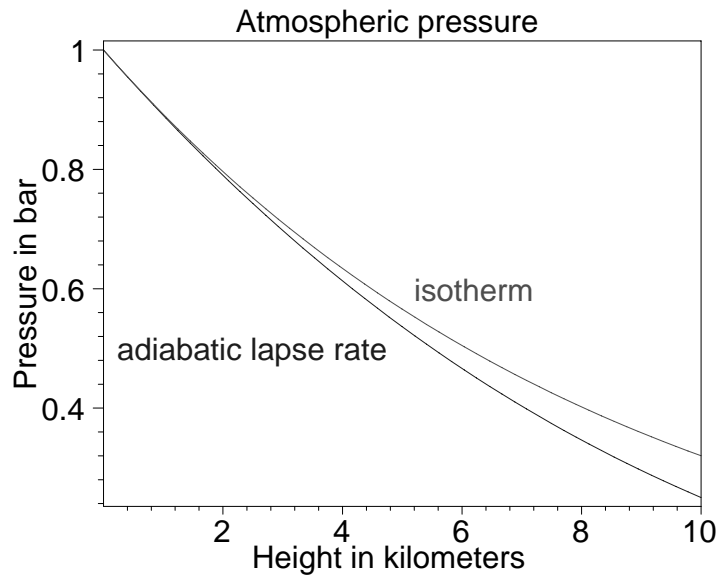
Note that in the limit $l \rightarrow 0$

$$\ln\left(1 - \frac{lz}{T_o}\right) \approx -\frac{lz}{T_o}$$

c: Substituting

$$m = 29/6.02/10^{-26} \text{ kg}, \quad g = 9.81 \text{ ms}^{-2}; \quad k = 1.381 \text{ J K}^{-1}, \quad l = 10^{-2} \text{ Km}^{-1}$$

gives the plot.



Problem 2:

The energy required is

$$90\text{kcal} = 377\text{kJ}$$

so the time required is

$$377000/600 = 628s = 10\frac{1}{2}\text{minutes}$$

Problem 3

For 5 heads or 5 tails the probability is

$$\frac{1}{2^5} = \frac{1}{32}$$

For 4 heads 1 tail or 1 tail 4 heads the probability is

$$\frac{1}{2^5} \frac{5!}{1!4!} = \frac{5}{32}$$

For 3 heads 2 tails or 2 heads 3 tails we have for the probability

$$\frac{1}{2^5} \frac{5!}{2!3!} = \frac{10}{32}$$

Problem set 3 2002

Problem 1:

a:

The number of ways that one can obtain 500 000 heads and an equal number of tails is

$$\Omega = \frac{10^6!}{(.5 \times 10^6!)^2}$$

Using Stirling's formula on the form

$$n! \approx n^n e^{-n} \sqrt{2\pi n}$$

we find

$$\Omega \approx \frac{(1000000)^{1000000} \exp(-1000000) \sqrt{2\pi 1000000}}{\left((500000)^{500000} \exp(-500000) \sqrt{2\pi 500000}\right)^2} = \frac{2^{1000000}}{\sqrt{500000\pi}}$$

b: The probability after 1 million coin tosses with a fair coin to get exactly 500 000 heads is then

$$\frac{1}{\sqrt{500000\pi}} = \frac{1}{1253}$$

This is in qualitative agreement with the fact that the width of the probability distribution is of the order $\sqrt{N} = 1000$

c: The entropy (in units of the Boltzmann constant k) of the state with 500 000 heads and an equal number of tails is

$$S/k = \ln \Omega = 10^6 \ln 2 - \ln(\sqrt{500000\pi})$$

The last term is small compared to the first so

$$S/k \approx 10^6 \ln 2$$

Problem 2:

a: An Einstein solid has on the average 1 vibrational quantum excited per oscillator. The multiplicity factor for an Einstein solid is

$$\frac{(N + q - 1)!}{(N - 1)!q!}$$

From Stirling's formula the entropy is thus

$$S = k[(N + q) \ln(N + q) - q \ln(q) - N \ln(N)] = Nk[2 \ln 2N - 2 \ln N]$$

The entropy per oscillator thus

$$\frac{S}{N} = 2k \ln 2$$

b: We express the energy in terms of the internal energy $U = \hbar\omega q$

$$S = k[(N + \frac{U}{\hbar\omega}) \ln(N + \frac{U}{\hbar\omega}) - \frac{U}{\hbar\omega} \ln(\frac{U}{\hbar\omega}) - N \ln(N)]$$

From

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

We find for the temperature substituting $q = N$ at the end

$$\frac{\hbar\omega}{kT} = \frac{T_E}{T} = \ln(N + \frac{U}{\hbar\omega}) - \ln \frac{U}{\hbar\omega} = \ln(N + q) - \ln(q) = \ln 2$$

or

$$T/T_E = 1/\ln 2$$

Problem 3:

a:

From the previous problem we have

$$\frac{T_E}{T} = \ln(N + q) - \ln(q)$$

we find for the solid with 1/2 quantum per oscillator

$$\frac{T_E}{T} = \ln 3 \Rightarrow T = \frac{T_E}{\ln 3}$$

For the one with two quanta per oscillator

$$\frac{T_E}{T} = \ln \frac{3}{2} \Rightarrow T = \frac{T_E}{\ln \frac{3}{2}}$$

b: On the average there are now

$$\frac{1}{2}(2 + \frac{1}{2}) = 1.25$$

quanta per oscillator. We find

$$\frac{T_E}{T} = \ln \frac{9}{5} \Rightarrow T = \frac{T_E}{\ln \frac{9}{5}}$$

Problem set 4 2002. Solution

Problem 1: From

$$S = Nk_B \left(\ln\left(\frac{V}{Nv_q}\right) + \frac{5}{2} \right)$$

$$v_q = \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

we see that the temperature for which the entropy would turn negative is given by

$$\frac{V}{Nv_q} = e^{-5/2}$$

or

$$T = \left(\frac{Ph^3 \exp(-\frac{5}{2})}{m^{3/2} k_B^{5/2} (2\pi)^{3/2}} \right)^{2/5}$$

Substituting $m = 4 \times 1.67 \cdot 10^{-27}$ kg, $h = 6.62 \cdot 10^{-34}$ Js, $k_B = 1.381 \cdot 10^{-23}$ JK⁻¹ we find $T = 0.68$ K.

Problem 2: The Sackur-Tetrode formula can be written

$$S = Nk_B \ln\left(\frac{\text{const.} VT^{3/2}}{N}\right)$$

If the entropy of stays constant in a system with a fixed number of particles

$$V_i T_i^{3/2} = V_f T_f^{3/2} = \text{const.}$$

With

$$T = \text{const.} PV$$

$$P_f V_f^\gamma = P_i V_i^\gamma$$

with $\gamma = 5/3$.

Problem 3:. If

$$v_q = \text{constant } T^{-\alpha}$$

we have for an isentropic process at constant N

$$VT^\alpha = \text{const}$$

or

$$V^{1+\alpha} P^\alpha = \text{const}$$

or

$$1 + \alpha = \frac{7\alpha}{5}$$

giving $\alpha = \frac{5}{2} = 2.5$.

Problem set 5 2002. Solution.

Problem 1:

a: Given that

$$U(S, V, N) = \text{const.} \cdot N \left(\frac{N}{V}\right)^{0.4} \exp\left(\frac{0.4 S}{Nk_B}\right)$$

we find

$$T = \left. \frac{\partial U}{\partial S} \right|_{N,V} = \frac{0.4U}{Nk_B}$$
$$P = - \left. \frac{\partial U}{\partial V} \right|_{S,N} = \frac{0.4U}{V}$$

comparing the two expressions we find

$$PV = 0.4U = Nk_B T$$

b: Substituting for U in the expression for P above

$$P = \text{const.} \cdot 0.4 \left(\frac{N}{V}\right)^{1.4} \exp\left(\frac{0.4S}{Nk_B}\right)$$

we find that for an adiabatic process ($S, N = \text{const}$)

$$PV^{1.4} = \text{const.}$$

Hence $\gamma = 1.4$.

Problem 2:

a: Since the cycle is run in the clockwise direction the device does the work and will serve as a heat engine.

b: The heat absorbed $B \Rightarrow C$ is

$$Q_H = C_P(T_C - T_B)$$

The heat expelled is

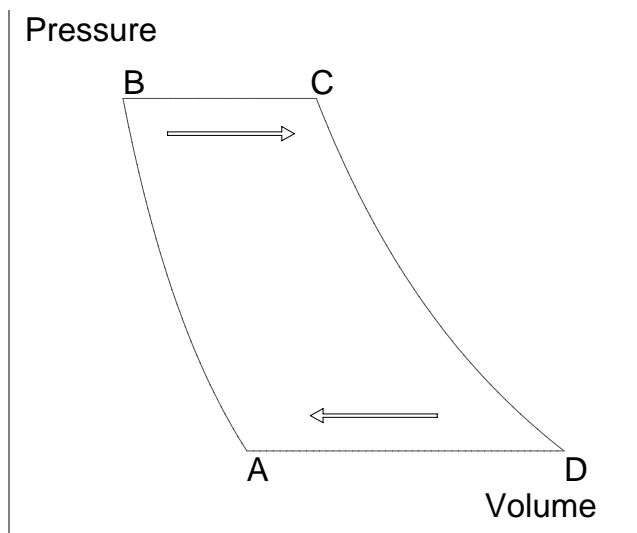
$$Q_C = C_P(T_D - T_A)$$

The coefficient of performance is thus

$$COP = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_D - T_A}{T_C - T_B}$$

Now, combining the adiabatic law

$$PV^\gamma = \text{const}$$



with the ideal gas law

$$PV = nRT$$

we find

$$T_B = T_A \left(\frac{P_B}{P_A} \right)^{(\gamma-1)/\gamma}$$

$$T_C = T_D \left(\frac{P_B}{P_A} \right)^{(\gamma-1)/\gamma}$$

so

$$COP = 1 - \left(\frac{P_A}{P_B} \right)^{(\gamma-1)/\gamma} = 1 - \left(\frac{1}{10} \right)^{1-1/1.4} = 0.48$$

Problem 3: We imagine that each gas is expanded isothermally to fill the whole volume

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_{V_1}^{V_1+V_2} \frac{n_1 R}{V} dV + \int_{V_2}^{V_1+V_2} \frac{n_2 R}{V} dV$$

Carrying out the integration we find

$$\Delta S = n_1 R \ln \frac{V_1 + V_2}{V_1} + n_2 R \ln \frac{V_1 + V_2}{V_2} = n_1 R \ln \frac{n_1 + n_2}{n_1} + n_2 R \ln \frac{n_1 + n_2}{n_2}$$

Substituting $n_1 = 1$, $n_2 = 2$ gives

$$\Delta S = R \ln 3 + 2R \ln \frac{3}{2}$$

Problem set 6 2002. Solution.**Problem 1:** From the Clausius Clapeyron equation we find

$$\frac{dp}{dT} = \frac{L}{T(V_l - V_g)}$$

For 1 kg of water $L = 80 * 1000 * 4.186 = 3.34 \times 10^5$ J. The change in volume of 1 kg of water is $1/1000 - 1/917 = -0.905 \times 10^{-4}$ m³. The change in pressure is $\Delta P = 99 \times 10^5$ N m⁻². The change in temperature is thus

$$\Delta T = \Delta P T (V_l - V_g) / L = -0.80 \text{K}$$

The melting temperature is lowered by a little less than one degree

Problem 2:

a: When the pressure of the water vapor is equal to the equilibrium vapor pressure the chemical potentials of gas and liquid are equal. From

$$d\mu = -sdT + vdP$$

we find that, since the neither the temperature nor the liquid chemical potential will change, the excess chemical potential in the vapor is approximately

$$\Delta\mu = \mu_g - \mu_l = v_g \Delta P$$

Since

$$v_g = \frac{k_B T}{P}$$

we find using $\Delta P / P = 0.1$

$$\Delta\mu = 0.1 k_B T$$

b: Using

$$v = \frac{4\pi r^3}{3}, \quad A = 4\pi r^2$$

for the volume and area of the drop we find for the excess Gibbs free energy

$$\Delta G = (\mu_l - \mu_g) \frac{4\pi r^3}{v_l} + \sigma 4\pi r^2$$

The maximum occurs when $\partial \Delta G / \partial r = 0$ or

$$r = \frac{2\sigma v_l}{\Delta\mu}$$

Since 1 kg of water contains $1000/18N_A$ molecules and has a volume of 10^{-3} m^3 we find using $R = N_A k_B = 8.315 \text{ J Mol}^{-1} \text{ K}^{-1}$, $\sigma = 0.073 \text{ Nm}^{-1}$

$$r = \frac{2 \times 0.073 \times 10^{-6} \times 18}{0.1 \times 8.315 \times 300} = 1.0 \times 10^{-8} \text{ m}$$

Problem 3:

a: We have

$$\mu = \frac{G}{N} = \frac{U}{N} - \frac{TS}{N} + \frac{PV}{N}$$

and for oxygen

$$\frac{U + PV}{N} \approx \frac{7}{2} k_B T$$

giving for the chemical potential of the gas in electron volt

$$\mu_g = \frac{7 \times 298 \times 1.381 \times 10^{-23}}{2 \times 1.602 \times 10^{-19}} - \frac{298 \times 205.14}{6.022 \times 10^{23} \times 1.602 \times 10^{-19}} = -0.547 \text{ eV}$$

b: Let N_a be the number of occupied sites. The number of ways N_a molecules can occupy N sites is

$$\Omega = \frac{N!}{(N_a)!(N - N_a)!}$$

The entropy is thus using Stirlings formula

$$S = k_B \ln \Omega \approx k_B (N \ln N - N_a \ln N_a - (N - N_a) \ln (N - N_a))$$

c: The Helmholtz free energy is

$$F = U - TS = N_a \epsilon - T k_B \ln \Omega \approx k_B (N \ln N - N_a \ln N_a - (N - N_a) \ln (N - N_a))$$

Giving for the chemical potential of the absorbed atoms

$$\mu_a = \frac{\partial F}{\partial N_a} = \epsilon - k_B T \ln \frac{N_a}{N - N_a}$$

What is the chemical potential of the absorbed oxygen under the conditions in part **b**?

d: Let $x = N_a/N$. At equilibrium the two chemical potentials must be equal or

$$\mu_g - \epsilon = k_B T \ln \left(\frac{x}{1 - x} \right)$$

solving for x we get

$$\frac{x}{1-x} = \exp\left(\frac{\mu_g - \epsilon}{k_B T}\right)$$

or with $k_B T = 298 \times 1.381 \cdot 10^{-23} / 1.602 \cdot 10^{-19} = 0.0257 \text{ eV}$

$$x = \frac{1}{\exp\left(\frac{\epsilon - \mu_g}{k_B T}\right) + 1} = \frac{1}{\exp\left(\frac{0.147}{0.0257}\right) + 1} = 0.0033$$

The fraction of occupied sites will be rather small at this temperature!

Review problems for final 2002. Solution

Problem 1: Let the energy levels be ϵ , $-\epsilon$ and 0. The partition function is

$$Z = e^{-\beta\epsilon} + 1 + e^{\beta\epsilon}$$

The probabilities are

$$P_1 = \frac{e^{-\beta\epsilon}}{Z}, \quad \frac{1}{Z}, \quad \frac{e^{\beta\epsilon}}{Z}$$

With $\epsilon = 0.1 \text{ eV}$, $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$, $k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ we find

$$P_1 = 0.0004, \quad P_2 = 0.0205, \quad P_3 = 0.9791$$

b: When the particles are distinguishable each particle can be in any of 3 state 9 states altogether:

system state	1st particle	2nd particle
1	1	1
2	1	2
3	1	3
4	2	1
5	2	2
6	2	3
7	3	1
8	3	2
9	3	3

If only one particle can be in each state and the particles are identical, system states 1,5 and 9 are forbidden. The pairs of system states (2,4), (3,7) and (6,8) are the same, leaving only three distinct system states 2,3 and 6.

If the particles are identical, but any number can occupy the same state the distinct system states are (1,2,3,5,6,9) leaving 6 states altogether.

Problem 2:

a: The partition function for a single oscillator is

$$Z = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + e^{-3\beta\hbar\omega} \dots = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

The probability tht there are exactly 3 quanta at temperature T is thus

$$P_3 = e^{-3\beta\hbar\omega} (1 - e^{-\beta\hbar\omega})$$

Substuting $\beta = 1/(1.381 \times 10^{-23} \times 300) \text{ J}^{-1}$, $\hbar\omega = 0.02 \times 1.602 \times 10^{-19} \text{ J}$ gives

$$P_3 = 0.053$$

b: The average thermal enrgy stored in the oscllator is

$$\langle E \rangle = \frac{1}{Z} \sum_{n=0}^{\infty} n\hbar\omega e^{-n\beta\hbar\omega} = -\frac{\partial}{\partial\beta} \ln Z = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = 0.017\text{eV}$$

Problem 3:

The most probable speed v_p , the mean spead $\langle v \rangle$ and the rms speed v_{rms} are given by, respectively

$$v_p = \sqrt{\frac{2k_B T}{m}}, \quad \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}, \quad v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

with $m = 32 \times 1.67 \times 10^{-27} \text{ kg}$, $T = 300\text{K}$, $k_B = 1.381 \times 10^{-23} \text{ JK}^{-1}$ we find

$$v_p = 394\text{ms}^{-1}, \quad \langle v \rangle = 444\text{ms}^{-1}, \quad v_{rms} = 482\text{ms}^{-1}$$

2002 Exams

Midterm October 4 2002.

Problem 1:

a.: The initial pressure in the chamber containing the gas is

$$P = RT/V = 8.31 \times 300/10^{-2} = 2.49 \times 10^5 \text{NM}^{-2} = 2.49\text{bar}$$

b.: Since the gas expands freely into the initially empty chamber no work is done and no heat produced. The internal energy is thus unchanged. Hence

the temperature is unchanged while the pressure is halved as the volume is doubled $\Rightarrow T = 300$, $P = 1.25$ bar

c: The final pressure is

$$P_f = P_i \left(\frac{V_f}{V_i} \right)^\gamma = 1.25 \times 2^\gamma = 3.97 \text{ bar}$$

if $\gamma = 5/3$ is used. We find for the final temperature

$$T_f = \frac{300 \times 3.97}{2.49} = 478 \text{ K}$$

d: The final pressure is larger than the initial pressure because the initial expansion involved no work, while in the final compression work was done on the gas, heating it.

Problem 2:

The number of mols is

$$n = \frac{PV}{RT} = \frac{10^5 \times 2 \times 10^{-3}}{8.315 \times 300} = .0801$$

Since the pressure is the same

$$n_1 R 300 / V = n_2 R 400 / V$$

combined with

$$n_1 + n_2 = 0.0801$$

gives $n_2 = 0.0343$, $n_1 = 0.0458$. We obtain

$$P = \frac{n_1 R T}{V} = \frac{0.0343 \times 8.315 \times 400}{10^{-3}} = 1.14 \text{ bar}$$

Problem 3:

a: The number of vibrational quanta per oscillator is

$$\frac{q}{N} = \frac{U}{N \hbar \omega} = \frac{1}{\exp(\frac{T_E}{T}) - 1} = 1.54$$

b: From

$$S = k_B [(N + q) \ln(N + q) - N \ln N - q \ln q]$$

$$\frac{S}{k_B N} = \left(1 + \frac{q}{N}\right) \ln\left(1 + \frac{q}{N}\right) - \frac{q}{N} \ln\left(\frac{q}{N}\right)$$

$$= \ln(1 + 1.54) - 1.54 \ln\left(\frac{1.54}{1}\right) = 1.70$$

c: The specific heat per mol is with $N = 3N_A$

$$\begin{aligned} C &= \frac{\partial U}{\partial T} = \frac{3N_A(\hbar\omega)^2 \exp(\frac{T_E}{T})}{k_B T^2 (\exp(\frac{T_E}{T}) - 1)^2} \\ &= 3R\left(\frac{1}{2}\right)^2 \frac{\exp(\frac{1}{2})}{(\exp(\frac{1}{2}) - 1)^2} = 2.93R \end{aligned}$$

Since the temperature is significantly larger than the Einstein temperature we expect a result close to $3R$, the Dulong and Petit value.

Second midterm 2002.Solution.

Problem 1:

Since the expansion is **free** no work is involved and there is no change in the internal energy. Hence there will be no change in the temperature.

a: The final temperature is $T_f = 300$ K. The final pressure is

$$P_f = \frac{(n_1 + n_2)RT}{V_1 + V_2}$$

Substituting

$$n_1 = 1, n_2 = 2, V_1 = V_2 = 10^{-3} \text{ m}^3, T = 300 \text{ K}$$

gives $P_f = 37.4$ bar

b: From

$$S = Nk_B \left[\ln \frac{V}{Nv_q(T)} + \frac{5}{2} \right]$$

we find

$$\begin{aligned} \Delta S &= (n_1 + n_2)R \left(\ln\left(\frac{V_1 + V_2}{(n_1 + n_2)N_A v_q}\right) + \frac{5}{2} \right) \\ &\quad - n_1 R \left(\ln\left(\frac{V_1}{n_1 N_A v_q}\right) + \frac{5}{2} \right) - n_2 R \left(\ln\left(\frac{V_2}{n_2 N_A v_q}\right) + \frac{5}{2} \right) \\ &= n_1 R \left(\ln\left(\frac{(V_1 + V_2)n_1}{V_1(n_1 + n_2)}\right) \right) + n_2 R \left(\ln\left(\frac{(V_1 + V_2)n_2}{V_2(n_1 + n_2)}\right) \right) = 1.41 \text{ J K}^{-1} \end{aligned}$$

c:The process is isothermal and doesn't depend on the form of $v_q(T)$. So, it doesn't matter if the gas is monatomic or diatomic!

Problem 2:

a:

$$COP = \frac{Q_C}{W} = \frac{1}{\frac{Q_H}{Q_C} - 1}$$

The second law implies that the entropy dumped into the hot reservoir must be at least as large as the entropy removed from the cold one. Thus

$$\frac{Q_H}{T_H} \geq \frac{Q_C}{T_C}$$

giving

$$COP \leq \frac{1}{\frac{T_H}{T_C} - 1}$$

b:

We have

$$W = \frac{Q_C}{COP}$$

Substituting

$$COP = \frac{1}{2(\frac{T_H}{T_C} - 1)}, \quad W = J * time, \quad Q_C = \alpha(T_H - T_C) * time$$

gives

$$J = \frac{2\alpha(T_H - T_C)^2}{T_C}$$

Solving for T_C gives rise to a quadratic equation. Putting

$$x = \frac{J}{4\alpha}$$

we find

$$\begin{aligned} 2xT_C &= T_H^2 + T_C^2 - 2T_H T_C \\ T_C &= T_H + x - \sqrt{x^2 + 2xT_H} \end{aligned}$$

Problem 3

a:

$$\Delta S = \int_i^f \frac{C_P dt}{T} = C_P \ln \frac{T_f}{T_i} = 4.18 * 18 \ln \frac{340}{298} = 10 \text{ J K}^{-1}$$

We find

$$\frac{\partial G}{\partial T} = -S = -S_i \Delta T - C_P \ln \frac{T}{T_i}$$

Hence

$$\Delta G = -S_i \Delta T - C_P \int_i^f dT \ln \frac{T}{T_i} = -S_i \Delta T - C_P (T_f \ln \frac{T_f}{T_i} - T_f + T_i)$$

For an **estimate** it is enough to include only the first term giving

$$\Delta G \approx 2.94 \text{ kJ}$$

A more accurate estimate involves evaluating the full expression giving

$$\Delta G \approx 3.15 \text{ kJ}$$

Sessional exam, December 10 2002, Solution

Problem 1:

a:

$$F = -Nk_B T \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + 1 \right) - \frac{aN^2}{V}$$

$$v_q = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{3/2}$$

The entropy is given by

$$S = - \left. \frac{\partial F}{\partial T} \right|_{N,V} = Nk_B \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + 1 \right) + \frac{Nk_B T}{v_q} \left. \frac{\partial v_q}{\partial T} \right|_{V,N}$$

or

$$S = Nk_B \left(\ln \left(\frac{V - Nb}{Nv_q} \right) + \frac{5}{2} \right)$$

b:

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_{N,V} = \frac{Nk_B T}{v_q} \left. \frac{\partial v_q}{\partial T} \right|_{V,N} = \frac{3Nk_B}{2}$$

c:

$$U = F + TS = -\frac{aN^2}{V} + \frac{3Nk_B T}{2}$$

When the gas is expanded from volume V to $2V$ the change in U will be

$$\Delta U = U_f - U_i = +\frac{aN^2}{2V}$$

To find how much work is done by the gas during the expansion we need

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

We have for the work

$$W = -\int_V^{2V} P dV = -\int_V^{2V} \left[\frac{Nk_B T}{V - Nb} - a\frac{N^2}{V^2} \right] dV$$

evaluating the integral we find

$$W = \frac{aN^2}{2V} - Nk_B T \ln \frac{2V - Nb}{V - Nb}$$

Problem 2:

To find the voltage we first calculate

$$\Delta G_{reaction} = \Delta G_{water} - \frac{1}{2}\Delta G_{oxygen} - \Delta G_{hydrogen} = -237.13 \text{ kJ mol}^{-1}$$

There are two N_A electrons circulation per formula unit mol

$$Voltage = \frac{237.13 \times 1000}{2 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-19}} = 1.23 \text{ Volt}$$

b: To find the change in the Gibbs free energy of the gases consider first an infinitesimal change at constant T, V

$$dG = Vdp$$

The change when the pressure changes by a finite amount is thus

$$\delta G = \int_{P_i}^{P_f} V dP = \int_{P_i}^{P_f} \frac{RT}{P} dP = RT \ln \frac{P_f}{P_i}$$

for the oxygen and hydrogen the Gibbs free energy per mol will thus **increase** by

$$\delta G_{oxygen} = \delta G_{hydrogen} = 8.315 \times 315 \times \ln 10 \times 10^{-3} = 5.7 \text{ kJ}$$

Neglecting the volume change of liquid water with pressure we find for the change in G with pressure

$$\delta G_{water} = 18.068 \times 10^{-6} \times 9 \times 10^5 \times 10^{-3} = 0.016 \text{ kJ}$$

c: The voltage of the cell will change by

$$\delta V = \frac{(1.5 \times 5.7 + 0.016) \times 1000}{2 \times 6.022 \times 10^{23} \times 1.602 \times 10^{-19}} = 0.044 \text{ Volt}$$

The voltage will **increase**.

Problem 3:

a: If the particles are distinguishable there are four possible states with energies, respectively, ϵ_1 , ϵ_2 and $\epsilon_1 + \epsilon_2$. Hence

$$Z = e^{-2\beta\epsilon_1} + e^{-2\beta\epsilon_2} + 2e^{-\beta(\epsilon_1 + \epsilon_2)}$$

The probability that one particle is in state 1 and one in state 2

$$P_{12} = \frac{2 \times e^{-\beta(\epsilon_1 + \epsilon_2)}}{Z}$$

b: If the particles are identical and two particles are forbidden from occupying the same state (fermions) there is only one allowed state the one with one particle in state 1 and the other in state two. We must not distinguish between the cases where the first is in 1 and the other in 2 and the reverse. The probability is thus

$$P_{12} = 1$$

c: If the particles are identical and several particles are allowed to occupy the same state (bosons) there are three possible states. The partition function is thus

$$Z = e^{-2\beta\epsilon_1} + e^{-2\beta\epsilon_2} + e^{-\beta(\epsilon_1 + \epsilon_2)}$$

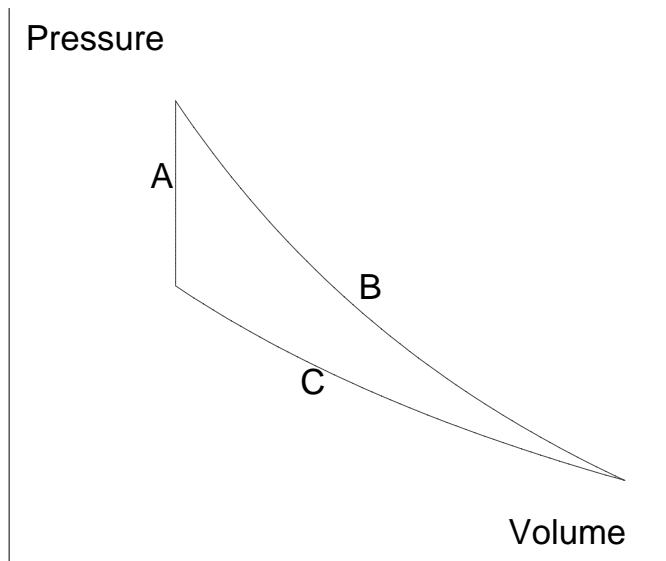
$$P_{12} = \frac{e^{-\beta(\epsilon_1 + \epsilon_2)}}{Z}$$

Problem 4:

a: See below for figure

b: There will be more work done by the gas during the adiabatic expansion than work done on the gas during the isothermal compression. So the system will work as an engine.

c:



- A** Since the volume is constant there is no work. The heat added to system is

$$Q_A = C_V \Delta T = \frac{3}{2} 8.315 \times 100 = 1.247 \text{ kJ}$$

- B** There is no heat added to system the work done by system is

$$W_B = \Delta U = C_V \Delta T = 1.247 \text{ kJ}$$

- C** There is no change in internal energy. The work done on system is equal to the heat given up by system.

$$W_C = -RT \ln \frac{V_f}{V_i} = \frac{3}{2} RT \ln \frac{4}{3} = 1.08 \text{ kJ}$$

Where we have used the adiabatic law

$$\frac{V_f}{V_i} = \left(\frac{300}{400} \right)^{3/2}$$

Problem 5:

- a:** The partial pressure of water vapor is

$$0.023/2 = 0.0115 \text{ bar}$$

The vapor pressure at temperature T is approximately

$$P = 0.0115 = 0.0023 \exp\left(\frac{44000}{8.315}\left[\frac{1}{293} - \frac{1}{T}\right]\right)$$

Solving for T we find $T = 282$. For the temperature to drop by 11 degrees the altitude has to be 1100 m.

b: The pressure drop of the water partial pressure is equal to the weight of water vapor in a column below

$$dP = -\frac{mgP}{k_B T} dz = \frac{mgP}{k_B (T_0 - 0.01z)} dz \approx -\frac{mgP}{k_B (T_{av})} dz$$

$$P \approx P_0 \exp\left(-\frac{mgz}{k_B T_{av}}\right) =$$

$$0.0115 \exp\left(-\frac{18 \times 1.673 \times 10^{-27} \times 9.81 \times 1100}{1.381 \times 10^{-23} 287.5}\right) = 0.0106 \text{ bar}$$

So the partial pressure will have dropped by 0.0009 bar or approximately 10%, which only will have a small effect on our result.

2001 Problems

Problem set 1

Problem 1:

a:

Let x be the temperature when the two readings are the same. From the conversion formula

$$x_F = \frac{9}{5}x_C + 32$$

Putting $x_F = x_C = x$ gives

$$x = -40$$

b:

$$T = \exp\left(-\frac{\ln(218) - 4.697}{3.917}\right) = 0.84 \text{ K}$$

Problem 2:

If the coefficient of linear expansion is α the coefficient of area expansion is

2α . The difference between the areas of the disk and the hole is the area of the gap:

$$A_{gap} = 2(\alpha_{steel} - \alpha_{Al})A\Delta T = 2(2.87 - 1.2)10^{-5}\pi\frac{(0.08^2)}{4}85 = 1.43 \cdot 10^{-5} \text{ m}^2$$

$$= 0.143 \text{ cm}^2$$

Problem 3:

We write

$$n = n_1 + n_2$$

where n_1 and n_2 be the number of moles of gas in the two compartments in the final state. We have with $T_1 = 273 + 15 = 288 \text{ K}$, $T_2 = 273 + 100 = 373 \text{ K}$, $V_1 = 200 \text{ cc}$, $V_2 = 300 \text{ cc}$, $P_i = 1 \text{ atm}$ initial pressure, $P_f =$ final pressure

$$P_i(V_1 + V_2) = (n_1 + n_2)RT_1$$

$$P_f(V_1) = n_1RT_1$$

$$P_f(V_2) = n_2RT_2$$

Eliminating n_1 and n_2 and solving for P_f we find

$$P_f = \frac{T_2 P_i (V_1 + V_2)}{V_2 T_1 + T_2 V_1}$$

Substituting numbers we find $P_f = 1.158 \text{ atm}$.

Problem set 2 2001. Solution

Problem 1:

a:

The heat required to warm 1 kg of water 1 degree is 1 kcal=4186 J. The work done on 1 kg of falling water is $100 \cdot 9.81 \text{ J}$

$$\Delta T = \frac{9.81 \cdot 100}{4186} = 0.234 \text{ K}$$

b:

The fraction of water evaporating is

$$\frac{9.81 \cdot 100}{4186 \cdot 540} = 0.00043$$

Problem 2:

$$3nR = 3 \frac{400}{63.54} 8.315 = 157 \text{ J K}^{-1}$$

The answer **c:** is closest.

Problem 3:

a:

Initially the temperature is

$$T = \frac{PV}{R}$$

after step 1 volume is

$$V_1 = 2^{-1/\gamma} V$$

$$T_1 = 2^{1-1/\gamma} T = 2^{1-1/\gamma} \frac{PV}{R} = 1.219T$$

after step 2

$$T_2 = 2T = \frac{2PV}{R}$$

after step 3 it is again

$$T = \frac{PV}{R}$$

b:

In step 1

$$Q_1 = 0$$

$$W_1 = U_1 - U_0 = \frac{fR}{2}(T_1 - T) = 0.5475PV$$

In step 2

$$W_2 = -P\Delta V = 2 * (2^{-1/\gamma} - 1) = -0.7810PV$$

$$Q_2 = \Delta U - W_2 = \frac{f}{2}(T_2 - T_1) - W_2 = 2.7335PV$$

In step 3

$$W_3 = 0$$

$$Q_3 = \Delta U = \frac{fR}{2}T = 2.5PV$$

c:

Total work

$$W = (0.5475 - 0.7810 + 0)PV = -0.2335 PV$$

$$Q = (0 + 2.7335 - 2.5)PV = +0.2335 = -W$$

in agreement with fact that $\Delta U = 0$ through cycle.

Problem set 3 2001

Problem 1:

Substituting the given formula for the logarithm of $n!$ into the expression for the multiplicity function of an Einstein solid gives

$$\ln(\Omega(q, N)) = (q + N - 1) \ln(q + N - 1) - (N - 1) \ln(N - 1) - q \ln(q) \\ - \frac{1}{2}(\ln(2 * \pi) + \ln(q + N - 1) - \ln((N - 1)q))$$

Evaluating this function for the logarithm of the multiplicity function of the compound solid

$$\ln(\Omega(2000, 6000))) = 4493.82$$

The number of ways 1000 quanta can be distributed among 3000 oscillators in both solids can be evaluated from

$$\ln(\Omega(1000, 3000)^2) = 4489.65$$

The probability for this is

$$\exp(4489.65 - 4493.82) = 0.0155$$

Problem 2:

a:

With the simplified formula

$$S = k_B \ln(\Omega(q, N)) = N k_B \left[\left(\frac{q + N}{N} \right) \ln \left(\frac{q + N}{N} \right) - \frac{q}{N} \ln \left(\frac{q}{N} \right) \right]$$

Substituting $N k_B = 3R$, $(q + N)/N = 4/3$, $q/N = 1/3$ gives

$$S = R(4 \ln(\frac{4}{3}) - \ln(\frac{1}{3})) = 18.70 \text{ J/K}$$

It was shown in class that

$$U = \hbar \omega q = \frac{N \hbar \omega}{\exp(\frac{\hbar \omega}{k_B T}) - 1}$$

with $q = N/3$, $T_E = \hbar \omega / k_B$ we find

$$\frac{1}{3} = \frac{1}{\exp \frac{T_E}{T} - 1}$$

or

$$T = \frac{T_E}{\ln 4} = 72\text{K}$$

b:

Problem 3:

Assuming there are 1000 characters on a page the probability of success is

$$\frac{10^6 * 10^{17}}{1000} \frac{1}{40^{1000}} \approx e^{-3600}$$

very small indeed!

Problem set 4 2001. Solution

Problem 1:

a:

Substituting

$$N_R = \frac{1}{2}(N + \frac{L}{l})$$

into

$$\frac{S}{k_B} = N \ln N - N_R \ln N_R - (N - N_R) \ln(N - N_R)$$

yields

$$\frac{S}{k_B} = N \ln N - \frac{N + \frac{L}{l}}{2} \ln \frac{N + \frac{L}{l}}{2} - \frac{N - \frac{L}{l}}{2} \ln \frac{N - \frac{L}{l}}{2}$$

We have

$$F = -T \left. \frac{\partial S}{\partial L} \right|_N = \frac{k_B T}{2l} \left(\ln \frac{N + \frac{N}{l}}{2} - \ln \frac{N - \frac{N}{l}}{2} \right)$$

which simplifies to

$$F = \frac{k_B T}{2l} \ln \frac{lN + L}{lN - L}$$

b:

The force needed to obtain a given length **increases** with temperature. Hence, when the force is constant the length decreases and the mass **moves up**.

c:

$$\mu = -T \frac{\partial S}{\partial N} = k_B T \left(\ln N - \frac{1}{2} \ln \frac{N + \frac{L}{l}}{2} - \frac{1}{2} \ln \frac{N - \frac{L}{l}}{2} \right)$$

This can be simplified to

$$\mu = k_B T \left(\ln \frac{1}{\sqrt{1 - \left(\frac{L}{Nl}\right)^2}} \right)$$

Problem 2:

a:

The internal energy per particle at height z is

$$U = N \frac{3}{2} k_B T + mgzN$$

into

$$v_q = \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

and

$$S = N k_B \left(\ln \frac{V}{N v_q} + \frac{5}{2} \right)$$

gives

$$S(U, N, V) = N k_B \left(\ln \left[\frac{V}{N^{5/2}} \left(\frac{4\pi m (U - Nmgz)}{3h^2} \right)^{3/2} \right] + \frac{5}{2} \right)$$

and

$$\mu = -T \frac{\partial S}{\partial N} \Big|_{U,V} = -k_B T \ln \frac{V}{N v_q} + mgz$$

b:

For the chemical potential to stay constant we must have

$$-k_B T \ln \frac{V}{N(z) v_q} + mgz = -k_B T \ln \frac{V}{N(0) v_q}$$

$$\ln \frac{N(z)}{N(0)} = -\frac{mgz}{k_B T}$$

or

$$N(z) = N(0) \exp \frac{-mgz}{k_B T}$$

For fixed T, V the pressure is proportional to N so

$$P(z) = P(0) \exp \frac{-mgz}{k_B T}$$

c:

At ground level

$$\mu = -k_B T \ln \frac{V}{N v_q} = -k_B T \ln \frac{V (2\pi m k_B T)^{3/2}}{N h^3}$$

$$\left. \frac{\partial \mu}{\partial T} \right|_{V, N} = -k_B \ln \frac{V}{N v_q} - \frac{3k_B}{2} < 0$$

since under atmospheric conditions $V/N \gg v_q$.

Thus, if the temperature decreases, N, V being constant, the chemical potential will **increase**!

d:

For the chemical potential to stay the same, if the temperature decreases as the altitude increases, the density has to decrease even more than predicted by the barometric formula in **c**:. Thus, the barometric formula overestimates the pressure at high altitudes!

Problem set 5 2001

Problem 1:

a: We have

$$du = \delta Q + \delta W$$

Substituting $\delta Q = C_V dT$ and $\delta W = -PdV$ gives

$$\delta Q = PdV + C_V dT$$

b:

From

$$P = P_1 + (V - V_1) \frac{P_2 - P_1}{V_2 - V_1}$$

we have along the straight line in the PV diagram

$$\frac{dP}{dV} = \frac{P_2 - P_1}{V_2 - V_1}$$

and

$$C_V dT = \frac{5}{2} n R dT = \frac{5}{2} (V dP + P dV)$$

We find

$$\frac{\delta Q}{dV} = \frac{7}{2} P + \frac{5}{2} V \frac{dP}{dV} = \frac{7}{2} (P_1 + (P_2 - P_1) \frac{V - V_1}{V_2 - V_1}) + \frac{5}{2} \frac{V}{V_2 - V_1} (P_2 - P_1)$$

For V close to V_1 , $\delta Q/dV$ will be negative. Since the gas is being compressed $\delta Q > 0$, i.e. the gas will be heated. At the other end the gas will be giving up heat. Putting $\delta Q = 0$ in the above expression gives

$$V_3 = \frac{7}{12} \frac{P_1 V_2 - P_2 V_1}{P_1 - P_2}$$

c:

We have

$$nR \frac{dT}{dV} = P + V \frac{dP}{dV} = P_1 + (V - V_1) \frac{P_2 - P_1}{V_2 - V_1} + V \frac{P_2 - P_1}{V_2 - V_1}$$

This expression is zero for

$$V_4 = \frac{1}{2} \frac{P_1 V_2 - V_1 P_2}{P_1 - P_2}$$

Substituting

$$V_1 = 1; V_2 = \frac{1}{2}; P_1 = 1; P_2 = 2$$

gives

$$V_3 = \frac{7}{8} \text{Liter}$$

$$V_4 = \frac{3}{4} \text{Liter}$$

i.e the heat flow does not change sign when the temperature is the maximum.

Problem 2:

a:

$$Q_H = nC_V(T_3 - T_2)$$

b:

$$Q_C = nC_V(T_4 - T_1)$$

c:

$$W = Q_H - Q_C$$

d: Substituting

$$\gamma = \frac{C_P}{C_V} = 1.4$$

$T_1 = 300$ K, $T_2 = 554$ K, $T_3 = 754$ K, $T_4 = 360$ K. into

$$e = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

yields

$$e = 58\%$$

Problem set 6 2001. Solution

Problem 1:

Let V_1 be the volume of the bottom partition. The Helmholtz free energy of the system is

$$F = -Nk_B T \left[\ln \frac{V_1}{Nv_q} + \ln \frac{V - V_1}{Nv_q} + 2 \right] + \frac{mgV_1}{A}$$

(a). The equilibrium height of the piston minimizes the free energy. We differentiate the free energy with respect to V_1

$$0 = \frac{\partial F}{\partial V_1} = -\frac{Nk_B T}{V_1} + \frac{Nk_B T}{V - V_1} + \frac{mgV_1}{A}$$

This equation could also be written down directly by noting that the pressure in the bottom partition is equal to the upper pressure $+mg/A$. Define

$$C \equiv \frac{Nk_B T A}{mg}$$

We find

$$-\frac{C}{V_1} + \frac{C}{V - V_1} + 1 = 0$$

or

$$V_1^2 - V_1(V + 2C) + CV = 0$$

With solution

$$V_1 = \frac{V + 2C}{2} \pm \sqrt{\frac{V^2}{4} + CV}$$

On physical grounds only the negative root is acceptable (the positive root gives rise to a negative volume for the upper partition). Substituting

$$h = \frac{V_1}{A}$$

for the height and the value of C

$$h = \frac{V}{2A} + \frac{Nk_B T}{mg} - \sqrt{\left(\frac{V}{2A}\right)^2 + \frac{VNk_B T}{mgA}}$$

(b). Since the top partition is at the vapor pressure, the pressure in the lower pressure will exceed the vapor pressure. Hence the lower partition contains only liquid.

Problem 2:

$$F(N, V, T) = -Nk_B T \left\{ \ln \left[\frac{V - Nb}{Nv_q} \right] + 1 \right\}$$

where

$$v_q = \frac{\text{constant}}{T^{5/2}}$$

and b is another positive constant.

a:

The pressure as a function of volume and temperature is thus

$$P = -\frac{\partial F}{\partial T} = \frac{Nk_B T}{V - Nb}$$

b:

The chemical potential is

$$\mu = \frac{\partial F}{\partial N} = -k_B T \ln \frac{V - Nb}{Nv_q} + \frac{bNk_B T}{V - Nb}$$

c:

We have for a given N and T

$$\frac{\partial V}{\partial P} = -\frac{Nk_B T}{P^2} < 0$$

Since the pressure decreases monotonically with the volume, there can be no co-existing phases \Rightarrow **there can be no phase transition!**

Problem 3:

We have

$$F(N_A, N_B, V, T) = -(N_A + N_B)k_B T \left\{ \ln \left[\frac{V - N_A b_A - N_B b_B}{(N_A + N_B)v_q} \right] + 1 \right\}$$

where b_A and b_B are positive constants and as before

$$v_q = \frac{\text{constant}}{T^{5/2}}$$

a:

$$P = -\frac{\partial F}{\partial V} = \frac{(N_A + N_B)k_B T}{V - N_A b_A - N_B B b_B}$$

Solving for V gives

$$V = N_A b_A + N_B B b_B + \frac{(N_A + N_B)k_B T}{P}$$

b: The entropy is

$$S = -\frac{\partial F}{\partial T} = (N_A + N_B)k_B \left\{ \ln \left[\frac{V - N_A b_A - N_B B b_B}{(N_A + N_B)v_q} \right] + 1 + (N_A + N_B)k_B T \frac{\partial v_q}{\partial T} \frac{1}{v_q} \right\}$$

which simplifies to

$$(N_A + N_B)k_B \left\{ \ln \left[\frac{V - N_A b_A - N_B B b_B}{(N_A + N_B)v_q} \right] + 7/2 \right\}$$

Problem set 7 2001. Solution

Problem 1:

The partition function for the system is

$$Z = [1 - \exp(-\beta \hbar \omega)]^{-N}$$

a:

$$\langle U \rangle = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{N \hbar \omega \exp(-\beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)}$$

which can be simplified to

$$\langle U \rangle = \frac{N \hbar \omega}{\exp(\beta \hbar \omega) - 1}$$

$$\langle U^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{N(\hbar \omega)^2 (N + \exp(\beta \hbar \omega))}{(\exp(\beta \hbar \omega) - 1)^2}$$

Hence

$$\langle U^2 \rangle - \langle U \rangle^2 = \frac{N(\hbar \omega)^2 \exp(\beta \hbar \omega)}{(\exp(\beta \hbar \omega) - 1)^2}$$

b: Using the formula for the specific heat

$$C = \frac{N(\hbar\omega)^2}{k_B T^2} \frac{\exp(\frac{\hbar\omega}{k_B T})}{(\exp(\frac{\hbar\omega}{k_B T}) - 1)^2}$$

c: The alternate way to calculate the specific heat is

$$C = \frac{\partial U}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial \langle U \rangle}{\partial \beta} = \frac{(N\hbar\omega)^2}{k_B T^2} \frac{\exp(\frac{\hbar\omega}{k_B T})}{(\exp(\frac{\hbar\omega}{k_B T}) - 1)^2}$$

which agrees with the result in **b**:

Problem 2: The oxygen and nitrogen concentrations at height h are given by

$$O_2(h) = O_2(0) \exp(-\beta m_{O_2} g h); \quad N_2(h) = N_2(0) \exp(-\beta m_{N_2} g h)$$

The ratio is thus

$$\frac{O_2(h)}{N_2(h)} = \frac{1}{4} \exp\left(\frac{g h (m_{N_2} - m_{O_2})}{k_B T}\right)$$

Substituting $m_{O_2} = 32 * 1.67 * 10^{-27}$ kg, $m_{N_2} = 28 * 1.67 * 10^{-27}$,
 $T = 273$ K, $k_B = 1.381 * 10^{-23}$ J/K, $g = 9.81$ m/s² gives

$$\frac{O_2(h)}{N_2(h)} = 0.229$$

Problem 3: If the two particles are in states with different labels the energy is zero and there are 6 such states. There are three states with energy $-\epsilon$.

a: The partition function of the system is

$$Z = 6 + 3 \exp(\beta\epsilon)$$

b: The mean energy of the system is

$$\langle U \rangle = \frac{-3\epsilon \exp(\beta\epsilon)}{6 + 3 \exp(\beta\epsilon)}$$

c: The free energy is

$$F = -k_B T \ln Z = -k_B T \ln(6 + 3 \exp(\frac{\epsilon}{k_B T}))$$

The entropy of the system is

$$S = -\frac{\partial F}{\partial T} = k_B \ln(6 + 3 \exp(\frac{\epsilon}{k_B T})) + \frac{\epsilon}{T(2 \exp(-\frac{\epsilon}{k_B T}) + 1)}$$

d: As $T \rightarrow 0$

$$\exp(\frac{\epsilon}{k_B T}) \rightarrow \infty; \quad \ln(6 + 3 \exp(\frac{\epsilon}{k_B T})) \rightarrow \ln(3) + \frac{\epsilon}{k_B T}; \quad \exp(\frac{-\epsilon}{k_B T}) \rightarrow 0$$

and

$$S \rightarrow k \ln(3) + \frac{\epsilon}{T} - \frac{\epsilon}{T} = k \ln(3)$$

This agrees with the fact that the lowest energy state has multiplicity = 3.
As $T \rightarrow \infty$

$$\exp(\frac{\epsilon}{k_B T}) \rightarrow 1; \quad \exp(-\frac{\epsilon}{k_B T}) \rightarrow 1; \quad T(2 \exp(\frac{-\epsilon}{k_B T}) + 1) \rightarrow \infty;$$

and

$$S \rightarrow k \ln(9)$$

At high temperatures all states are equally likely and there are 9 available states!

Problem set 8 2001. Solution

Problem 1:

For an ideal gas

$$C_V = \frac{f}{2} N k_B = \frac{f P V}{2 T}$$

Substituting into the formula for the energy variance gives

$$\langle U^2 \rangle - \langle U \rangle^2 = \frac{f}{2} P V k_B T$$

or

$$\sigma = \sqrt{\frac{f}{2} P V k_B T} = \sqrt{\frac{5}{2} 10^5 \times \frac{4\pi}{3} 10^{-9} \times 1.38 \times 10^{-23} \times 300} = 2.08 \times 10^{-12} J$$

The internal energy is

$$\frac{5}{2} N k_B T = \frac{f}{2} P V = \frac{5}{2} \times 10^5 \frac{4\pi}{3} 10^{-9} = 1.05 \times 10^{-3} J$$

giving for the ratio

$$\frac{\sigma}{U} = 2 \times 10^{-9}$$

Problem 2:

a: Substituting

$$F = -Nk_B T \left[\ln \frac{c(V - Nb)T^{5/2}}{N} + 1 \right] - a \frac{N^2}{V}$$

into

$$P = -\frac{\partial F}{\partial V}|_{T,N} = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

Gives

$$G = F + PV = -Nk_B T \left[\ln \frac{c(V - Nb)T^{5/2}}{N} + 1 \right] - \frac{aN^2}{V} + \frac{NVk_B T}{V - Nb} - \frac{aN^2}{V}$$

which can be simplified to

$$G = -Nk_B T \ln \frac{c(V - Nb)T^{5/2}}{N} - \frac{N^2 b}{V - Nb} k_B T - \frac{2aN^2}{V}$$

b:

We have

$$\mu = \frac{\partial F}{\partial N} = k_B T \left[\ln \frac{c(V - Nb)T^{5/2}}{N} + 1 \right] - \frac{Nb k_B T}{V - Nb} - k_B T - 2a \frac{N}{V}$$

which after some simplification yields

$$G = N\mu = -Nk_B T \ln \frac{c(V - Nb)T^{5/2}}{N} - \frac{N^2 b}{V - Nb} k_B T - 2a \frac{N^2}{V}$$

which is the same result as before

c: With

$$\beta = \frac{1}{k_B T}$$

$$\beta F = -N \left[\ln \frac{ck_B^{5/2}(V - Nb)}{N\beta^{5/2}} + 1 \right] - a \frac{\beta N^2}{V}$$

The internal energy U is given by

$$U = -\frac{\partial Z}{Z \partial \beta} = \frac{\partial \beta F}{\partial \beta} = \frac{5N}{2\beta} - a \frac{N^2}{V}$$

or

$$U = \frac{5}{2}Nk_B T - a \frac{N^2}{V}$$

Problem 3

a:

The work in expanding the vapor is

$$PV = nRT$$

The molecular weight of water is 18g so 1kg water contains

$$n = 1000/18 = 55.55 \text{ mol}$$

The work is then

$$55.55 \times 8.31 \times 373 / 4.18 = 41.2 \text{ kCal}$$

which is $41.2/540 = 7.62\%$ of the total.

b: From the Clausius Clapeyron equation

$$\frac{\Delta P}{\Delta T} \approx \frac{L}{TV}$$

$$\Delta T = \frac{\Delta PVT}{L} = \frac{\Delta P nRT^2}{PL} = \frac{55.55 \times 8.31 \times 373^2}{2 \times 540 \times 4.18 \times 1000} = 28.5^\circ \text{C}$$

Problem 4:

The coefficient of performance of the heat pump is

$$COP = \frac{Q_H}{Q_H - Q_C} \leq \frac{T_H}{T_H - T_C} = \frac{273 + 80}{80} = 4.41$$

So the heat pump would use 4.4 times less heat (but it would cost more to install!).

Problem 5:

The excess Gibbs free energy of the droplet is $\sigma A = 4\sigma\pi r^2$. The number of molecules in the droplet is with r in meters noting that there 1 m^3 of water has a mass of 10^6 g (or contains 55 555 mol of water)

$$\frac{4\pi r^3 N_A 10^6}{3 \times 18}$$

so the excess free energy per particle is

$$3 \frac{\sigma}{r \times 55\,555 \times N_A} = \frac{3 \times 0.073}{10^{-6} \times 55\,555 \times 6.022 \times 10^{23}} = 0.655 \times 10^{-23} \text{ J}$$

which is small compared to

$$k_B T = 0.404 \times 10^{-20} \text{ J}$$

2001 Exams

Midterm October 10 2001. Solution

Problem 1:

The initial and final volumes on the right side are

$$V_{ri} = \frac{RT_i}{P_i}; \quad V_{rf} = \frac{RT_i}{2P_i}$$

a:

$$P_f = 2P_i = 2 \text{ bar}$$

b: The left volume is after the compression

$$V_{lf} = \frac{3}{2}V_i$$

The temperature on the left side is thus

$$T_{lf} = \frac{P_f V_{lf}}{R} = 3T_i = 900 \text{ K}$$

c: The work done on the right chamber is

$$W = - \int_{V_{ri}}^{V_{rf}} P dV = RT_i \ln \frac{V_{ri}}{V_{rf}} = 1729 \text{ J}$$

d:

On the left side

$$Q_L = W + \Delta U_r = W + \frac{5}{2}R(T_{rf} - T_{ri}) = 14.2 \text{ kJ}$$

On the right side

$$Q_R = -W = -1729 \text{ J}$$

Problem 2:

$$S = Nk_B \left\{ \ln \left[\frac{V}{N} \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

a:

If $P \Rightarrow 2P$ and V is unchanged, $T \Rightarrow 2T$. Hence

$$\Delta S = \frac{nR}{2} \ln 8$$

b: If $P \Rightarrow 2P$ and T is unchanged, $V \Rightarrow V/2$. Hence

$$\Delta S = -nR \ln 2$$

Problem 3:

At the Einstein temperature the expected number of quanta is

$$q = \frac{N}{e - 1}$$

Substitute into the formula for the entropy

$$S = k_B [(N + q) \ln(N + q) - N \ln N - q \ln q]$$

Using

$$\ln(N + q) = \ln\left(1 + \frac{q}{N}\right) + \ln(N)$$

The entropy per oscillator is then

$$s = \frac{S}{N} = k_B \left(\left(1 + \frac{q}{N}\right) \ln\left(1 + \frac{q}{N}\right) - \frac{q}{N} \ln \frac{q}{N} \right) = k_B \left(\frac{e}{e - 1} - \ln(e - 1) \right)$$

plugging in numbers we find

$$s = 1.04 k_B$$

Second midterm November 5 2001. Solution.

Problem 1:

a:

The working substance absorbs heat when expanding at constant pressure

$$Q_H = C_P(T_3 - T_2)$$

The heat expelled is

$$Q_C = C_P(T_4 - T_1)$$

We have for the thermodynamic efficiency

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

b: During an adiabatic process

$$PV^\gamma = \text{const}$$

Using the ideal gas law $PV = nRT$ we find

$$P^{1-\gamma}T^\gamma = \text{Const}$$

Hence

$$\left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{T_2}{T_1}\right)^\gamma = \left(\frac{T_3}{T_4}\right)^\gamma$$

or

$$\frac{T_4}{T_1} = \frac{T_3}{T_2}$$

Substituting into the formula for the efficiency

$$e = 1 - \frac{\frac{T_4}{T_1} - 1}{\frac{T_3}{T_2} - 1} = 1 - \frac{T_1}{T_2} = 1 - \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}$$

c: Substituting $P_1 = 1$ bar, $P_2 = 8$ bar, $\gamma = 1.4$ gives

$$1 - \left(\frac{1}{8}\right)^{0.4/1.4} = 0.45$$

Problem 2:

$C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$. The entropy of one mol of argon at 298 K was given as 154.84 J/K and $\Delta T = 4$ K.

a: The change in energy is

$$\Delta U = C_V \Delta T = 49.9 \text{ J}$$

b: The change in entropy is

$$\Delta S = \int_i^f \frac{dQ}{T} \approx \frac{C_P \Delta T}{T_{\text{average}}} = 0.28 \text{ J/K}$$

c: The change in enthalpy is

$$\Delta H = C_P \Delta T = 83.15 \text{ J}$$

d:

$$\Delta G = -S \Delta T = -619 \text{ J}$$

Problem 3:

a:

The heat given up by the hot water is equal to the heat gained by the cold water. Let T be the final temperature of the mixture

$$10(90 - T) = 6(T - 10)$$

giving $T = 60^\circ \text{C}$.

b: The initial temperatures and the final temperature measured in Kelvin are, respectively 363 K, 283 K and 333 K

$$\begin{aligned} \Delta S &= M_1 c_P \int_{363}^{333} \frac{dT}{T} + M_2 c_P \int_{283}^{333} \frac{dT}{T} = \\ 10 \times 4180 \ln \frac{333}{363} + 6 \times 4180 \ln \frac{333}{283} &= 475 \text{ J/K} \end{aligned}$$

Sessional exam, December 13 2001, Solution

Problem 1:

a:

For a diatomic gas we expect C_P for a mole to be close to

$$\frac{7}{2}R = 29.10 \text{ J K}^{-1}$$

So $C_P = 29.38 \text{ J K}^{-1}$ is most likely to be correct.

b: If the gas is heated at constant pressure, it will expand, and will have to do work against the outside pressure to do this. This means that more heat will have to be provided than if the gas is heated at constant volume.

Problem 2:

$$F = -\frac{\pi^2 V}{45 \hbar^3 c^3 \beta^4}$$

where $\beta = 1/kT$, c is the speed of light and \hbar is Planck's constant divided by 2π .

a: The entropy is

$$S = - \left. \frac{\partial F}{\partial T} \right|_V = - \frac{\partial \beta}{\partial T} \frac{\partial F}{\partial \beta} = \frac{1}{k_B T^2} \frac{4\pi^2 V}{45\hbar^3 c^3 \beta^5} = \frac{4\pi V k_B^4 T^3}{45\hbar^3 c^3}$$

The pressure is

$$P = - \frac{\partial F}{\partial V} = \frac{\pi^2 k_B^4 T^4}{45\hbar^3 c^3}$$

b: The internal energy is

$$U = F + TS = \frac{(-1 + 4)\pi V k_B^4 T^4}{45\hbar^3 c^3} = \frac{\pi V k_B^4 T^4}{15\hbar^3 c^3}$$

The enthalpy is

$$H = U + PV = \frac{4\pi V k_B^4 T^4}{45\hbar^3 c^3}$$

c:

$$G = H - TS = \frac{(4 - 4)\pi V k_B^4 T^4}{45\hbar^3 c^3} = 0$$

The number of photons will be fluctuating. At equilibrium the expected number $\langle N \rangle$ of photons is given by the condition that $\langle N \rangle$ minimizes the free energy

$$\frac{\partial F}{\partial N} = \mu = 0$$

Problem 3:

a: We have

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Giving

$$W = - \int_i^f P dV = -nRT \ln \left(\frac{V_f - nb}{V_i - nb} \right) - an^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

Substituting $n = 0.2$ mole, $V_i = 10^{-3}$ m³, $V_f = 10^{-4}$ m³, $a = 0.5$ J m³, $T = 500$ K, $b = 3 \times 10^{-5}$ m³ mole⁻¹, $R = 8.315$ J mole⁻¹ K⁻¹ gives

$$W = 1961 - 180 = 1781 \text{ J}$$

b: In an ideal gas the internal energy is independent of the density of the gas and depends only on the temperature. The first law then requires that for an isothermal process

$$0 = \Delta U = \Delta W + \Delta Q$$

from which it follows that the work done in compressing the gas equals to the heat expelled. For the imperfect gas

$$\Delta U \neq 0$$

and the magnitudes of heat and work will be different.

Problem 4:

From the Clausius-Clapeyron equation

$$dT = \frac{PT\Delta V}{L}$$

Consider 1 kg chunk of lead. Let ρ_L and ρ_S be the density of liquid and solid lead, respectively. The volume increases upon melting by

$$\Delta V = \frac{1}{\rho_L} - \frac{1}{\rho_S}$$

Substituting numbers

$$dT = \frac{99 \times 10^5 \times (327 + 273) \times 10^{-4} \left(\frac{1}{1.065} - \frac{1}{1.101} \right)}{24500} = 0.744^\circ$$

At higher pressure more work is required for the expansion at melting. Hence, the melting temperature increases.

Problem 5:

a: We have

$$COP = \frac{Q_h}{W} = \frac{1}{1 - \frac{Q_c}{Q_h}}$$

The entropy loss of the outside must be less than the entropy gain inside for the total entropy not decrease.

$$\frac{Q_c}{T_c} \leq \frac{Q_h}{T_h}$$

from which it follows that

$$\frac{T_h}{T_c} \leq \frac{Q_h}{Q_c}$$

or

$$COP < \frac{1}{1 - \frac{T_c}{T_h}}$$

b: We have (assuming ideal performance)

$$Q_h = \alpha * (T_h - T_c) = COP * W = \frac{W * T_h}{T_h - T_c}$$

we get a quadratic equation for T_h with solution

$$T_h = T_c + \frac{W}{2\alpha} \pm \sqrt{\frac{W}{\alpha} + \frac{W^2}{4\alpha^2}}$$

Assuming that $T_h > T_c$ we must choose the positive root.

2000 Exams

The problem sets assigned that year were from the text by Schroeder and are not included here.

First midterm 2000. Solution.

Problem 1:

Subscript t,b =top, bottom. In all cases the bubble satisfies the ideal gas law

$$PV = nRT$$

a:

If the bubble rises at constant temperature

$$P_b V_b = P_t V_t \Rightarrow V_t = V_b \frac{P_b}{P_t} = 6 \text{ mm}^3$$

b:

If the bubble rises adiabatically

$$P_b V_b^\gamma = P_t V_t^\gamma$$

From this we find

$$\Rightarrow V_t = V_b \left(\frac{P_b}{P_t} \right)^{1/\gamma} = 3.6 \text{ mm}^3$$

c:

Heat is supplied to the isothermal bubble and not to the adiabatic one. Hence, the former is warmer and thus bigger.

d:

$S = \text{constant}$ for an adiabatic process. From the Sackur Tetrode law for the entropy

$$\Rightarrow \frac{V}{v_Q} = \text{const}$$

Since $v_Q \propto T^{-3/2}$ and using the ideal gas law

$$\Rightarrow VT^{3/2} = \text{const} \Rightarrow V^{5/2}P^{3/2} = \text{const.} \Rightarrow PV^{5/3} = \text{const}$$

Hence

$$\Rightarrow \gamma = 5/3$$

Problem 2:

$$\beta V = \beta \frac{4\pi r^3}{3} = \frac{\pi h d^2}{4}$$

a:

$$d = \sqrt{\frac{\beta 16 r^3}{3h}}$$

b

$$d = 0.123 \text{ mm}$$

c:

The volume of the bulb is $4\pi r^3/3 = 21 \text{ mm}^3$. Assuming a 10 cm column its volume is $100\pi d^2/4 = 0.4 \text{ mm}^3$, which is much smaller than the volume of the bulb.

Problem 3:

The mass of the balloon plus the mass of the hot air must be less than the mass of the displaced air for the balloon to rise.

a:

$$M + \frac{mPV}{RT_H} = \frac{mPV}{RT_C}$$

$$T_H = \frac{1}{\frac{1}{T_C} - \frac{RM}{mPV}}$$

b: Substituting numbers gives $T=366$ K

c:

Subtract the mass

$$\frac{mPV_P}{RT_C}$$

of the air displaced by the payload from the mass M to get the effective pay-load.

Second midterm 2000. Solution.

Problem 1:

a:

Applying Stirling's formula and $S = k_B \ln \Omega$ to

$$\Omega = \frac{(N+q-1)!}{q!(N-1)!}$$

gives

$$S = k_B \{ (N+q-1) \ln(N+q) - q \ln q - (N-1) \ln(N-1) \}$$

Since $N \gg 1$, we can approximate this as

$$S = k_B [(N+q) \ln(N+q) - q \ln q - N \ln N]$$

b:

We need to express S as a function of U and N

$$S = k_B \{ (N + \frac{U}{\hbar\omega}) \ln(N + \frac{U}{\hbar\omega}) - \frac{U}{\hbar\omega} \ln \frac{U}{\hbar\omega} - N \ln N \}$$

giving

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B}{\hbar\omega} \ln(1 + \frac{N\hbar\omega}{U})$$

and

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N} = -k_B \ln(1 + \frac{U}{N\hbar\omega})$$

and finally

$$T = \frac{\hbar\omega}{k_B \ln(1 + \frac{N\hbar\omega}{U})}$$

and

$$\mu = -\frac{\hbar\omega \ln(1 + \frac{U}{N\hbar\omega})}{\ln(1 + \frac{N\hbar\omega}{U})}$$

c: when

$$T = \frac{\hbar\omega}{k_B}$$

$$1 = \ln(1 + 1/q)$$

$$q = \frac{N}{e - 1}$$

Substituting into formula for S, there is a common factor of Nk_B and we find

$$s = \frac{S}{Nk_B} = 1.04$$

Problem 2:

The quantities $s_i(T)$ and $v_q(T)$ in the expression

$$S = Ns_i(T) + Nk_B[\ln \frac{V}{Nv_q(T)} + \frac{5}{2}]$$

do not change during the processes under consideration. We have $N_A k_B = R$

a:

The initial entropy is

$$S_i = 2N_A s_{i,He}(T) + 2N_A k_B [\ln \frac{V_i}{2N_A v_{q,He}(T)} + \frac{5}{2}] + N_A s_{i,O_2}(T) + N_A k_B [\ln \frac{V_i}{N_A v_{q,O_2}(T)} + \frac{5}{2}]$$

The final entropy is

$$S_f = 2N_A s_{i,He}(T) + 2N_A k_B [\ln \frac{2V_i}{2N_A v_{q,He}(T)} + \frac{5}{2}] + N_A s_{i,O_2}(T) + N_A k_B [\ln \frac{2V_i}{N_A v_{q,O_2}(T)} + \frac{5}{2}]$$

The change in entropy is thus

$$\Delta S = S_f - S_i = 3N_A k_B \ln 2 = 3R \ln 2$$

b:

$$\Delta S = -3N_A k_B \ln 2 = -3R \ln 2$$

c:

The initial entropy is now

$$S_i = 2N_A s_{i,He}(T) + 2N_A k_B \left[\ln \frac{V_i}{2N_A v_{q,He}(T)} + \frac{5}{2} \right] + N_A s_{i,He}(T) + N_A k_B \left[\ln \frac{V_i}{N_A v_{q,He}(T)} + \frac{5}{2} \right]$$

while the final entropy is

$$S_f = 3N_A s_{i,He}(T) + 3N_A k_B \left[\ln \frac{2V_i}{3N_A v_{q,He}(T)} + \frac{5}{2} \right]$$

giving

$$\Delta S = R \ln \frac{32}{27}$$

note that while there is no longer an entropy change due to mixing, there is an entropy change to equalize the pressure!

Sessional Examination, December 2000, Solution

1:

a:

Since $C_V = C_P - R$ and

$$f = \frac{C_V}{2R}$$

$$f = 2 * (29.38 - 8.315) / 8.315 = 5.067$$

b:

O_2 at room temperature is a diatomic gas. Hence we expect 3 translational and 2 rotational degrees of freedom i.e. $f = 5$. The very slight excess means that the vibrational degrees of freedom are almost completely frozen in.

c: For CH_4

$$f = 2 * (35.31 - 8.315) / 8.315 = 6.49$$

With 3 rotational 3 translational degrees of freedom we would expect $f = 6$, the excess means that the vibrational energies are not completely frozen in at room temperature.

2:

a:

$$\mu_{old} = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]$$

After half the molecules have been pumped out

$$\mu_{new} = -kT \ln \left[\frac{2V}{N} \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \right]$$

Hence the change is

$$\Delta\mu = \mu_{new} - \mu_{old} = -kT \ln 2$$

b:

The change is now

$$\Delta\mu = -2kT_{old} \ln \left[\frac{cV}{N} (2T_{old})^{5/2} \right] + kT_{old} \ln \left[\frac{cVT_{old}^{3/2}}{N} \right] = -5kT_{old} \ln 2 - kT_{old} \ln \left[\frac{cVT_{old}^{5/2}}{N} \right]$$

or

$$\Delta\mu = -2kT_{old} \ln \left[\frac{32cVT_{old}^{5/2}}{N} \right]$$

c:

If $p = 1/2$ we must have $\exp(\epsilon - \mu/kT) = 1$. Since $\Delta\mu = -kT \ln 2$ we must have

$$p = \frac{1}{e^{(\epsilon - \mu - \Delta\mu)/kT} + 1} = \frac{1}{2 + 1} = \frac{1}{3}$$

It doesn't matter if the gas is monatomic or diatomic.

3:

a:

From the van der Waals equation we have

$$\frac{PV}{NkT} = 1 - \frac{aN}{VkT} + \frac{abN^2}{V^2kT} + \frac{Pb}{kT}$$

Substitute the critical values

$$CF = \frac{P_c V_c}{NkT_c} = 1 - \frac{27}{3 \times 8} + \frac{27}{8 \times 9} + \frac{1}{8} = \frac{3}{8} = .375$$

Alternatively, we can substitute directly into the expressions for the critical quantities

$$\frac{P_c V_c}{NkT_c} = \frac{\frac{a}{27b^2}(3Nb)}{N \frac{8a}{27b}} = \frac{3}{8}$$

b:

We have

$$V_C = CF \times \frac{NkT_c}{P_c} = \frac{CF \times R \times T_c}{P_c} = .274 \times 8.315 \times 647220.6 \times 10^5 = 66.8 \times 10^{-6} m^3$$

c:

When fitting to T_c, P_c we have to solve

$$a = 27b^2 P_c, \quad a = \frac{27}{8} b k T_c$$

for a and b giving

$$a = \frac{27k^2 T_c^2}{64P_c}, \quad b = \frac{kT_c}{8P_c}$$

using $k = R/N_a$ and the provided values for the constants gives

$$a = 1.53 \times 10^{-48} Nm^4; \quad b := 5.06 \times 10^{-29} m^3$$

When fitting P_c, V_c we have

$$b = \frac{V_c}{3N_a} = 3.70 \times 10^{-29} m^3$$

giving

$$a = 27b^2 P_c = 8.13 \times 10^{-49} Nm^4$$

The discrepancy between the two fits suggests that the van der Waals model of a fluid only offers a qualitative description and is not particularly good for a quantitative theory.

4:

a:

The voltage of a battery containing n cells

$$V = -\frac{n\Delta G}{2eN_a} = \frac{6 \times 394 \times 1000}{6.022 \times 10^{23} \times 2 \times 1.602 \times 10^{-19}} = 12.27 \text{ Volt}$$

b:

The heat absorbed by the battery per formula unit per mole is

$$T\Delta S = \Delta H - \Delta G > 0$$

Since the battery absorbs heat when discharged, waste heat is produced when battery is charged.

c:

Since

$$\frac{\partial \Delta G}{\partial T} = -\Delta S = -\frac{\Delta H - \Delta G}{T}$$
$$\Delta V = n\Delta T \frac{\Delta H - \Delta G}{2TeN_a} \approx 0.2V$$

The voltage **increases** when heated!

5:

a:

Under ideal operating conditions

$$T_h \Delta S_h = Q_h; T_c \Delta S_c = -Q_c, Q_h - Q_c = W; \Delta S_h + \Delta S_c = 0$$

$$COP = Q_h/W = \frac{T_h}{T_h - T_c}$$

b:

The energy required is $1/COP = (T_h - T_c)/T_h = 0.068 \text{ kWh}$ if it is $0^\circ C$ outside. If it is $-40^\circ C$ the cost would be $60/293 = 0.20 \text{ kWh}$

c:

For the air conditioner the COP would be $Q_c/W = T_c/(T_h - T_c) = 293/15$. So the energy cost would be $15/293 = 0.051 \text{ kWh}$ under ideal circumstances. Of course, ideal circumstances cannot be achieved, but if energy prices keep going up, heat pumps may turn out to be a good idea!