Problem 3.3   [FOR ASSIGNMENT 2; max 10 points]

Isothermal vs. adiabatic expansion.

A cylinder filled with nitrogen gas expands from 10 to 100 litres. It is initially at atmospheric pressure and room temperature ($T_i = 298$ K).

   (a) Determine the work done by the gas and its final temperature, assuming the expansion process is isothermal.

   (b) Perform the same calculation for an adiabatic expansion.

   (c) Explain the differences between the results of (a) and (b).

a)   If the process is isothermal, the temperature will be constant throughout. ($T = 298$ K) The work follows:

$$W = -\int_{V_I}^{V_F} P \, dV$$

Note: $10 L = 0.01 m^3$ $100 L = 0.1 m^3$

$$W = -\int_{0.01}^{0.1} \frac{nRT}{V} \, dV$$

$$T = 298$$

given $P_I = 1 atm = 101.325 \, kPa_1$

$$n = \frac{0.01 \times 101.325 \times 10^3}{R \times 298} = 0.41 \, mol$$

$$W = -\int_{0.01}^{0.1} \frac{0.41 \, R \times 298}{V} \, dV$$

$$= -1015 \left[\ln(V) \right]_{0.01}^{0.1}$$
$$= -1015 \ln\left(\frac{0.1}{0.01}\right)$$
$$= -2339 \, J$$

Thus the gas did $2339 J$ of work.

b) For an adiabatic process we understand the process to follow:

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

where γ is the adiabatic exponent:

$$\gamma = \frac{f+2}{f}$$

We understand that at 298K, nitrogen gas (N_2), a linear molecule will have three translational degrees of freedom and two rotational degrees of freedom. At 298K it is assumed that $f_{vib} = 0$

∴ Initial conditions tell us: 0.16

$$101.325 \times 10^3 \times (0.01)^{\frac{5+2}{5}} = 160$$

Thus:

$$W = -\int_{0.01}^{0.1} \frac{0.16}{V^{\frac{2}{5}}} \, dV$$

$$= -160 \left[-\frac{5}{2} V^{-\frac{2}{5}} \right]_{0.01}^{0.1}$$

$$= -1519.1 \, J$$

Thus the gas did 1519.1J of work.

c) As displayed on the graph to the right, we find process a and b to be isothermal and adiabatic respectively. As observed on the graph, given the adiabatic process crosses isotherms, we find the work done by the gas to be much larger for the isothermal process. This directly supports the calculated values and is a direct result the adiabatic process being unable to transfer heat with its surroundings, meaning less work was required.
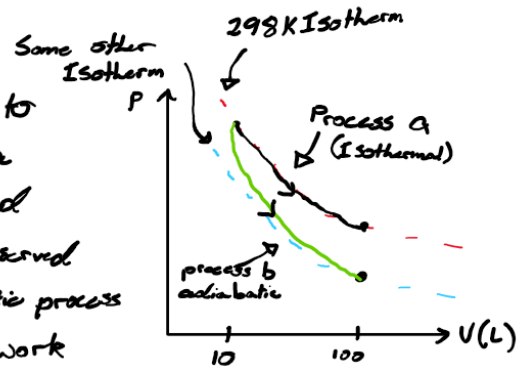
The isothermal process however continuously transferred heat with its surroundings, meaning more work had to be done to counteract this loss.

Problem 3.5   [FOR ASSIGNMENT 2; max 10 points]

Oxygen, copper and thermal equilibrium.

A rigid and thermally isolated container holds 2 mol of oxygen at a pressure of 1 bar and temperature of 300 K. A small block of 100 g of copper at 800 K is introduced in the container. You can assume that the volume of the copper block is negligible with respect to the volume of the container, and that O_2 is an ideal gas. The specific heat capacity of copper is 387 J/kg·K.

(a) What is the final equilibrium temperature of the gas?

(b) What is the final equilibrium pressure of the gas?

a)

O_2 :   Moles $= 2$ mol

$T_i = 300$ k

$P = 100\ 000$ Pa

Copper   mass $= 100$g $= 0.1$ kg

$T_I = 800$k

$C_v = 387 \dfrac{J}{kg\, k}$ (Not rigid bodie implies Constat Volume)

As O_2 is being considered as an ideal gas, we find.

$C_v = \dfrac{f}{2} R$

At relatively low temperatures, we will assume O_2 to have 5 degrees of freedom:

$O = O$ 3 translational
                  2 rotational
            No vibrational   as $T < 100$ k

$$C_v = \frac{f}{2}R = \frac{5}{2}R \; J/_{kg\,k}$$

Thus, as $\quad Q_{O_2} = -Q_{cu} \quad \Rightarrow \quad n\,C_v\,\Delta T = mc\,\Delta T$

$$2 \times \frac{5}{2}R \times (T_f - 300) = -0.1 \times 387 \times (T_f - 800)$$

final temperatures must equate.

$$5R\,T_f - 1500\,R = -38.7\,T_f + 30960$$

$$T_f = \frac{30960 + 1500R}{5R + 38.7}$$

$$= 541.1 \; K$$

b) We must first find the volume of the rigid system:

Initially
$$P = 100\ 000\ Pa$$
$$T = 300K$$
$$n = 2\ mol$$
$$\therefore V = \frac{nRT}{P} = \frac{2 \times R \times 300}{100\ 000}$$
$$= 0.05m^3$$

Thus as $V_I = V_F$ (Rigid body)
Finally:
$$T = 541.1\ K$$
$$n = 2\ mol$$
$$V = 0.05m^3$$

$$P = \frac{nRT}{V} = \frac{2 \times R \times 541.1}{0.05}$$

$$= 179950.4\ Pa$$
$$= 179.95\ kPa$$

Problem 4.4 [FOR ASSIGNMENT 2; max 10 points]

Entropy changes from heating water.

We want to increase the temperature of one kilogram of liquid water with an initial temperature of 273 K. Assume that the pressure is constant and that the heat capacity of water is $c_P = 4.2$ J/g·K at all temperatures.

What is the change in entropy of the water, of the heat reservoir(s) used to heat the water, and the universe:

(a) if the water is brought in contact with a heat reservoir at $T_1 = 373$ K?

(b) if the water is brought in contact with a heat reservoir at $T_1 = 323$ K and then with a heat reservoir at $T_2 = 373$ K (after reaching thermodynamic equilibrium with the first reservoir)?

Additionally:

(c) Prove that the entropy of the universe always increases regardless of the temperature of the reservoir when it is in thermal contact with the water (assuming there is a finite temperature difference between the water and the reservoir). What does this tell you about the process of heat exchange?

(d) Explain how the water might be heated from 273 K to 373 K with a minimal change in entropy of the universe.

a) Water:

$$mass = 1\,kg = 1000\,g$$
$$T_I = 273\,k$$
$$C_p = 4.2\,J/gk$$

373k reservoir:

An ideal heat reservoir has infinite thermal conductivity and heat capacity, such that the system when in contact experiences a constant 373 k   i.e $T_f = 373k$

We further understand that the water will experience an entropy change given by:

$$\Delta S = \int_{T_I}^{T_f} \frac{dQ}{T} = \int_{T_I}^{T_f} \frac{mC_p dT}{T}$$

$$= \int_{273}^{373} \frac{4.2 \times 1000}{T}\,dT = 4200\left[\ln(T)\right]_{273}^{373}$$

$$= 4200\ln\left(\frac{373}{273}\right)$$

$$= 1310.8\,J/k$$

Thus the water experienced a entropy increase of 1310.8 J/k

Given the reservoir reasoning previously outlined, $Q_{res} = -Q_{water}$:

$$Q_{water} = mc_p \Delta T = 4200 \times 100 = 420 kJ$$
$$\therefore Q_{res} = -420 kJ$$

For an ideal reservoir:

$$\Delta S = \frac{Q}{T} = \frac{-420\ 000}{373}$$
$$= -1126\ J/k$$

Thus the reservoir experienced a 1126 J/k decrease in entropy.

ΔS for the universe is the net ΔS:

$$\Delta S_{uni} = \Delta S_{res} + \Delta S_{water}$$
$$= -1126 + 1310.8$$
$$= 184.8\ J/k$$

Thus the universe experienced a net 184.8 J/k entropy increase.

b) For water:

$$\Delta S = \int_{T_I}^{T_F} \frac{dQ}{T} + \int_{T_I}^{T_F} \frac{dQ}{T}$$

First reservoir   Second reservoir

$$\Delta S = \int_{273}^{323} \frac{4200}{T} dT + \int_{323}^{273} \frac{4200}{T} dT$$

Note T_I for second
is temp of first as
equilibrium was made.

$$\Delta S = 4200 \left(\ln\left(\frac{323}{273}\right) + \ln\left(\frac{373}{323}\right) \right)$$

$$= 1310.8 \; J/k \quad \left(For \; water \right)$$

First reservoir:

$$\Delta S_1 = \frac{-4200(323-273)}{323}$$

$$= -650.15 \; J/k \qquad \text{Note -ve}$$

Signs as
$Q_{res} = -Q_{water}$

Second reservoir

$$\Delta S_2 = \frac{-4200(373-323)}{373}$$

$$= -563.0 \; J/k$$

Thus the net reservoirs entropy is:

$$\Delta S_{res} = \Delta S_1 + \Delta S_2$$
$$= -1213.15 \ J/K$$

Thus the total entropy change of the universe is:

$$\Delta S_{uni} = \Delta S_{res} + \Delta S_{water}$$
$$= -1213.15 + 1310.8$$
$$= 97.65 \ J/K$$

c) For some water of temperature T_w and mass m, and reservoir of temperature T_r we find:

Thus:

$$\Delta S_{net} = \Delta S_w + \Delta S_r$$

For the case where $T_r > T_w$

$$-Q_r = Q_w : \quad (\text{Heat from reservoir to water})$$

$$\Delta S_{net} = \frac{Q_w}{T_w} - \frac{Q_r}{T_r} \quad \text{Since } \Delta S = \frac{Q}{T}$$

as $T_r > T_w$, $\frac{1}{T_w} > \frac{1}{T_r}$ and thus

$$\Delta S > 0$$

If $T_w > T_r$

$$Q_r = -Q_w \quad (\text{Heat from water to reservoir})$$

$$\Delta S = \frac{Q_r}{T_r} - \frac{Q_w}{T_w}$$

as $T_w > T_r$, $\frac{1}{T_r} > \frac{1}{T_w}$ thus:

$$\Delta S > 0$$

Thus in both temperature cases

$$\Delta S > 0$$

d) To reduce the enthalpy increase is to make the process more reversible. This being said, we understand that a process is more reversible if the irreversibilities are reduced, namely those caused by the large temperature difference between the water and reservoir. We have just shown that an intermediate 323K reservoir reduced the total change in enthalpy from 184.85J/k to 96.65J/k.
This is a result of it becoming closer to a quasi-static process. Further, we can suggest that to minimise the entropy increase, more reservoirs must be added, with infinite reservoirs behaving like a quasi-static purpose.

Entropy of mixing.

Mixing is usually irreversible, but since entropy is a state function we can calculate the change in entropy of mixing by considering a reversible mixing process.

An example of reversible mixing is shown in Figure 2. Consider mixing a gas of molecules of types w (the corresponding number of molecules being n_w) and b (likewise, the corresponding number of molecules is n_b). Initially, these molecules are separated by a combination of two pistons. The leftmost piston is permeable to w molecules but not b molecules, and the rightmost piston is permeable to b molecules but not w molecules. In combination, these two pistons are not permeable to either molecule. However, we can move the leftmost piston and let the gas of b

molecules expand leftwards. Then we can move the rightmost piston and let the gas of w molecules expand rightwards. At the end of this process, the molecules occupy the entire volume $V_w + V_b$. The final state has the same temperature and pressure as the initial state, but the atoms are now mixed. If the process is sufficiently slow, then we can reverse the process from the system's current state back towards the system's initial state without introducing any thermodynamic gradients—hence, the mixing is reversible.
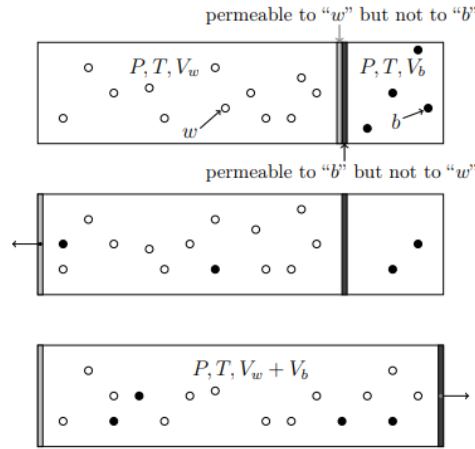

Figure 2: Reversible mixing example. The initial state is in the top diagram. The middle diagram is after moving the leftmost piston allowing b molecules to move left. The bottom diagram, which is the final mixed state, is after moving the rightmost piston allowing w molecules to move right.

(a) Assume that the gas is ideal and derive the following expression for the entropy of mixing:
$$\Delta S_{\text{mix}} = -Nk_B[x \ln x + (1 - x) \ln(1 - x)], \tag{1}$$
where $N = n_w + n_b$, $x = n_b/N$, and k_B is the Boltzmann constant.

(b) Derive Equation 1 using combinatorics.

(HINT: See Problem 4.5(d). Consider the $N-$circles in the bottom panel in Figure 2 and calculate the number of ways n_b indistinguishable molecules of them can be filled with black).

(c) Approximations to Equation 1 can be applied in cases of a dilute mixture (a mixture where, for example, n_w is much larger than n_b, i.e., when $x \ll 1$). Show that in this case:
$$\Delta S_{\text{mix}} = -Nk_B[x \ln x - x]. \tag{2}$$

(HINT: consider the Taylor Series for $\ln(1 - x)$).

(d) Suppose you drop a small crystal in a liquid. Considering the entropy formula in Equation 2, argue that some atoms in the crystal will spontaneously mix (i.e., dissolve) in the liquid regardless of the compositions of the liquid and crystal.

a) Consider gas w:

$$\Delta S_w = Nk \ln\left(\frac{V_F}{V_s}\right) = n_w k \ln\left(\frac{V_w + V_b}{V_w}\right)$$

$$= -n_w R \ln\left(\frac{V_w}{V_w + V_b}\right)$$

gas b:

$$\Delta S_b = -n_b k \ln\left(\frac{V_b}{V_w + V_b}\right)$$

$$\Delta S_{net} = \Delta S_w + \Delta S_b$$

$$= -n_w k \ln\left(\frac{V_w}{V_w + V_b}\right) - n_b R \ln\left(\frac{V_b}{V_b + V_w}\right)$$

$$= n_w k \ln\left(\frac{V_w}{V_w + V_b}\right) + n_b R \ln\left(\frac{V_b}{V_b + V_w}\right)$$

Given the gas is ideal, $PV = nRT$

$$\frac{V_w}{V_w + V_b} = \frac{\frac{n_w RT}{P}}{\frac{n_w RT}{P} + \frac{n_b RT}{P}} = \frac{n_w}{n_w + n_b}$$

$$\frac{V_b}{V_b + V_w} = \frac{n_b}{n_b + n_w}$$

$$= -n_w \, k \ln\left(\frac{n_w}{n_w + n_b}\right) - n_b k \ln\left(\frac{n_b}{n_b + n_w}\right)$$

$$\equiv (N - n_b) \, k \ln\left(\frac{N - n_b}{N}\right) - n_b k \ln\left(\frac{n_b}{N}\right)$$

$$= -(N - n_b) k \ln(1 - x) - n_b k \ln(x)$$

$$= -Nk\left(\frac{N - n_b}{N} \ln(1 - x) + \frac{n_b}{N} \ln(x)\right)$$

$$= -N k_B\left((1 - x) \ln(1 - x) + x \ln(x)\right)$$

QED

b)

Consider the general expression for multiplicity:

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

Notice for our case, $(N - n_b)! = n_w!$ thus:

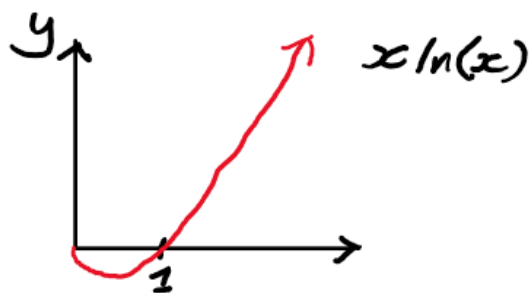$$\Omega(N, n_b) = \frac{N!}{n_b! \, n_w!}$$

Given $S = k_B \ln \Omega$ and:

Stirlings approximation $\ln N! \approx N \ln N - N$

$$S = k_B \ln\left(\frac{N!}{n_b! \, n_w!}\right)$$

$$= k_B\left(\ln(N!) - \ln(n_b! \, n_w!)\right)$$

$$= k_B\left(N \ln N - N - \ln(n_b!) - \ln(n_w!)\right)$$

$$= k_B\left(N \ln N - N - (n_b \ln(n_b) - n_b) - (n_w \ln(n_w) - n_w)\right)$$

$$= k_B\left(N \ln N - N - (n_b \ln(n_b) - n_b) - ((N-n_b)\ln(N-n_b) - (N-n_b))\right)$$

$$= k_B N\left(\ln(N) - 1 - x\ln(n_b) + x - \underset{\sim}{(N-n_b)}\ln(N-n_b) + 1 - x\right)$$

$$= N k_B\left(\ln(N) - x\ln(n_b) - (1-x)\ln(N-n_b)\right)$$

$$= N k_B\left(\ln(N) - x\ln(xN) - (1-x)\ln((1-x)N)\right)$$

$$= N k_B\left(\ln(N) - x\ln x - x\ln N - (1-x)\ln(1-x) - (1-x)\ln(N)\right)$$

$$= N k_B\left((1-x)\ln(N) - x\ln(x) - (1-x)\ln(1-x) - (1-x)\ln(N)\right)$$

$$= -N k_B\left(x\ln(x) + (1-x)\ln(1-x)\right) = \Delta S_{mix}$$

QED

c) In the case $x \ll 1$ we notice:

$x \ln(x)$ will be decently funky such that the term must continue to be considered.

Lets now consider $(1-x)\ln(1-x)$
we notice $(1-x)$ goes to 1 as $x \ll 1$.
Lets further evaluate $\ln(1-x)$,

The taylor series expansion is as follows:

$$\ln(1-x) = -\sum_{n=1}^{\infty} \frac{x^n}{n} = -x - \frac{x^2}{2} - \frac{x^3}{3} \ldots$$

As $x \ll 1$, the higher order terms $x^2, x^3 \ldots$ become negligible. Thus $\ln(1-x) \approx -x$

$\therefore \Delta S_{mix} = -N k_B \left(x \ln(x) + (1)(-x) \right)$
$\qquad = -N k_B \left(x \ln(x) - x \right)$

Alternatively by the same reasoning:

$$(1-x)\ln(x) \neq (1-x)(-x)$$
$$= -x + x^2$$

as $x \ll 1$, x^2 is negligible.

QED.

d) When some small crystal is dropped in a liquid, we can follow its process by naming a crystal molecule n_c and liquid n_l with $n_c + n_l = N$.

Given x represents a focus molecule ratio to the whole system, we will define

$$x = \frac{n_c}{N}$$

In this way, we notice n_c to be very small as the crystal is very small. As previously justified, this means $\frac{n_c}{N} \ll 1$, $x \ll 1$ and thus the entropy follows:

$$\Delta S_{min} = -Nk_B \left(x\ln x - x \right)$$

This shows that irrespective of the crystal and liquid structure, some mixing entropy must exist even for small samples and thus some of the crystal will dissolve.