

Hour Exam 2 - Solutions Spring 2024

1. (10 pts) Consider rolling a six-sided die.

a) (2) What is the probability of rolling a one? A two? Any face on the die?

Solution: $P(1) = 1/6$, $P(2) = 1/6$, $P(\text{any side}) = 1/6$

b) (2+1) What is the average value of a roll? Is it possible to roll the average value?

Solution: $1(1/6) + 2(1/6) + 3(1/6) + 4(1/6) + 5(1/6) + 6(1/6) = 3.5$ No, it is not possible to roll this.

c) (2+1) Now suppose I instead roll two six-sided dice and add the results. What is the average value of a roll now? Is it possible to roll this number?

Solution: $2(1/36) + 3(2/36) + 4(3/36) + 5(4/36) + 6(5/36) + 7(6/36) + 8(5/36) + 9(4/36) + 10(3/36) + 11(2/36) + 12(1/36) = 7$ Yes, it is possible to roll this.

d) (1+1) Suppose instead of rolling just one or two dice, I roll many dice and add up my results. What function does the probability distribution approach as I increase the number of dice to infinity? What theorem guarantees this?

Solution: It will approach a normal (gaussian) distribution by the central limit theorem.

2. (10 pts) Consider a box of volume $2V$, with $2M$ cells, each of volume V_0 (size of an N_2 or O_2 molecule).

a) (1+1+1) Initially, let N identical O_2 molecules be on the left side of the box, so that the right half of the box is empty. **How many** microstates are there for this configuration ($W_{O_2 \text{ before}}$)? How about for N identical N_2 molecules on the right ($W_{N_2 \text{ before}}$)? **How many** microstates $W_{total,unmixed}$ total are there when N_2 and O_2 are unmixed?

Solution: $W_{O_2 \text{ left}} = W_{N_2 \text{ right}} = \frac{M!}{(M-N)!N!}$; $W_{total,unmixed} = \frac{M!}{(M-N)!N!} * \frac{M!}{(M-N)!N!}$

b) (1+1+1) Next, let the N identical O_2 molecules be anywhere in the box. **How many** microstates are there for this configuration ($W_{O_2 \text{ anywhere}}$)? **How about** $W_{N_2 \text{ anywhere}}$ for N identical N_2 molecules? **How many** microstates W_{mixed} for N_2 and O_2 combined?

Solution: $W_{O_2 \text{ anywhere}} = W_{N_2 \text{ anywhere}} = \frac{2M!}{(2M-N)!N!}$; $W_{mixed} \approx \frac{2M!}{(2M-N)!N!} * \frac{2M!}{(2M-N)!N!}$

Note that the latter formula is approximate and works only if $M \gg N$. The reason is that if both N_2 and O_2 are together in the box, each has only $2M-N$ cells available (some are occupied by the other type of molecule), but O_2 and N_2 are distinguishable! Each type of molecule can occupy any cell in the box, but not all cells are available due to being occupied by the other type of molecule. Why do you think

$$W_{mixed} = \frac{2M!}{(2M-N)!N!} * \frac{(2M-N)!}{(2M-2N)!N!}$$

Would be a better answer?

c) (2) **Write a formula** for the change of entropy upon mixing O₂ on the left with N₂ on the right so they fill the whole box afterwards, in terms of W_{mixed} and $W_{total,unmixed}$?

Solution:

$$\begin{aligned}\Delta S &= S_{mixed} - S_{total,unmixed} \\ &= k_B \ln(W_{mixed}) - k_B \ln(W_{total,unmixed}) \\ &= 2k_B \ln\left(\frac{2M!(M-N)!}{M!(2M-N)!}\right)\end{aligned}$$

d) (2) For M=10 and N=5, **what is** the entropy difference in Joules/Kelvin?

Solution: $\Delta S = 2k_B \ln\left(\frac{20!5!}{10!15!}\right) \approx 2 \times 1.38 \times 10^{-23} \left(\frac{J}{K}\right) \ln(62) \approx +1.1 \times 10^{-22} \text{ J/K}$

3. (10 pts) In a steam locomotive, steam pushes a piston inside a cylinder to drive wheels. Thus the vapor at pressure P does work by moving the piston to increase volume by dV . Let's assume the expansion is slow enough so that the gas remains at the same temperature as the cylinder, $T=400$ K. Assume the gas is 'ideal.'

a) (2) **Write down** the formula for mechanical work dw in terms of pressure P and volume change dV .

Solution: $dw = PdV$

b) (2+2) Assuming steam obeys the ideal gas law, **eliminate pressure** as a variable in (a), and **integrate** both sides (assuming T and n are constant) to obtain w when the volume increases from V_1 to V_2 .

Solution: $PV=nRT \Rightarrow dw = \frac{nRT}{V} dV$; $w = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\left(\frac{V_2}{V_1}\right)$. (By assuming T is constant, heat must be flowing into the gas when it does work on the surroundings; this increases the entropy of the gas.)

c) (2) If 20 moles of gas expand to twice the original volume in the cylinder, what is the work done in Joules?

Solution: $w = 20 \cdot 8.31 \cdot 400 \cdot \ln(2) \approx 46,000 \text{ J}$. Note that if the piston moves once per second, that's 46 kW, a respectable power output. A horse can do about 1 kW.

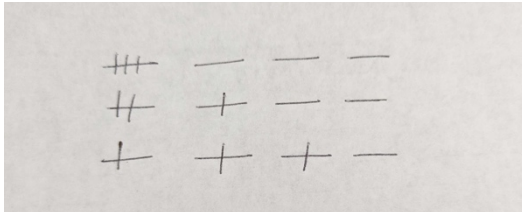
d) (2) Using the formula $\Delta S = w/T$ that relates work w at constant temperature to entropy change ΔS , **by how much** did the entropy of the gas increase while doing this work?

Solution: $\Delta S = w/T \approx 46000/400 \approx 115$ Joules/K. A gas that expands without heat flowing in will experience a decrease in temperature while it does work, and its energy will decrease. But here we assume T is constant, so heat must be flowing into the gas to keep T constant.

4) (10 pts) A simple model for estimating the microcanonical partition function Z : Consider $N=4$ identical molecules, represented as horizontal lines, and $k=3$ energy packets with energy ϵ . Assume these 3 packets are completely randomly distributed over the molecules

a) (2) **Draw** all possible cases for distributing 3 energy packets in the 4 identical molecules.

Solution :



(b) (2) **Plot** the probability ρ_j that a molecule has energy E_j . [Hint : How many molecules have 3 energy packets? 2? 1? 0?]



Solution:

c) (1+1) What are the **two** rigorously derived general formulas for Z that relate microscopic parameters like W_j and E_j to macroscopic parameters like the free energy?

Soln : $Z = \sum_j W_j e^{-\beta E_j} = e^{-\beta F}$

d) (2+1+1) Assuming the energy per packet is $\epsilon = k_B T$, (equipartition), and realizing that there are $W_j=6$ molecule states with energy 0ϵ , etc., **calculate** a numerical value for Z in the example in (a) using a formula in (c). **How many** microstates are occupied? **Calculate** the free energy F at 300 K using (c).

Solution:

$Z = 1xe^{-3} + 1xe^{-2} + 4xe^{-1} + 6xe^{-0} \approx 7.65$ microstates; $F = -RT \ln(Z) = -8.31 \text{ J/K/mole} * 300 \text{ K} * \ln(7.65) \approx -5 \text{ kJ/mole}$ (and of course correspondingly smaller by Avogadro's number per individual molecule).