

In Lectures 10 - 14 the subject of entropy has been introduced and covered from a basic statistical mechanics perspective. Specifically, the concepts of microstates and macrostates have been developed and related to changes in entropy via Boltzmann's formula ($S = k \ln (W)$). The following questions are designed to further the students' understanding of a variety of (inter-related) topics including: microstates, macrostates, combinations, permutations, probability, changes in entropy and the 2^{nd} law.

Q1 In Lectures 10 and 11 the game of poker was used both to introduce the concepts of combinations and permutations, and to serve as a *rough* analogy to the ideas of microstates and macrostates in thermal physics[†]. We can treat each hand of poker (dealt from a standard deck of 52 cards comprising 4 suits ($\P, \clubsuit, \diamondsuit, \diamondsuit)$ of 13 cards each) as being a particular microstate and we can write down a number of possible macrostates:

- (i) royal flush (eg, $A \bigstar$, $K \bigstar$, $Q \bigstar$, $J \bigstar$, $10 \bigstar$),
- (ii) full house (eg, $5\bigstar$, $5\bigstar$, $5\blacktriangledown$, $3\diamondsuit$, $3\bigstar$)
- (iii) four of a kind (eg, 5♣, 5♦, 5♥, 5♠, 8♠),
- (iv) a pair (eg, $Q \spadesuit$, $Q \clubsuit$, $5 \heartsuit$, $7 \blacklozenge$, $9 \bigstar$), and
- (v) 'junk' (eg, $2 \bigstar$, $A \bigstar$, $Q \heartsuit$, $J \blacklozenge$, $7 \bigstar$)

For this question we are concerned only with hands that fall in categories (i) - (v) (i.e. we are not considering a straight flush or other 'winning combinations' of cards). Hence a 'junk' hand is a hand that does not fall in categories (i) - (iv).

- (a) How many possible microstates are there for a standard deck of cards (comprising 4 suits of 13 cards each)? (Note that (A♠, K♠, Q♠, J♠, 10♠) and (K♠, A♠, J♠, 10♠, A♠) represent the same hand of cards).
- (b) Determine the number of microstates that contribute to each of macrostates (i) (v) given above and *hence* write down which of (i) (v) above is the most likely and the least likely macrostate.
- (c) Why is it not correct to use the expression $S = k \ln(W)$ to determine the thermodynamic entropy of each hand of cards?

Q2. The entropy of an object somewhere in the Universe changes by -10 JK^{-1} as the result of some arbitrary process. From the second law of thermodynamics which of the following is a possible value for the entropy change of the rest of the Universe:

(i)
$$-10 \text{ JK}^{-1}$$
, (ii) 0 JK^{-1} , (iii) $+ 10 \text{ JK}^{-1}$, (iv) $+ 20 \text{ JK}^{-1}$?

Account for your choice(s).

[†] As stressed repeatedly throughout the lectures (and in Set 3 of the lecture notes), we need to be *exceptionally careful* with definitions and the use of analogies when discussing entropy and the 2nd law. Remember that we spent some time discussing just why the idea of a room becoming more 'disordered' (i.e. 'messy') is NOT an example of an increase in thermodynamic entropy. The same arguments hold for a deck of cards.

Q3. Calculate the change in the total entropy of the Universe for the following processes:

- (i.) A block of mass 1 kg, temperature 100°C and heat capacity 100 JK⁻¹ is placed in a lake whose temperature is 10°C;
- (ii.) The same block at 10°C is dropped into the lake from a height of 10 metres;
- (iii.) A block of mass 1 kg, heat capacity 100 JK⁻¹ and at 10°C absorbs a photon of light ($\lambda = 600 \text{ nm}$);
- (iv.) Two such blocks at 10°C and 100°C are joined together;
- (v.) The block at 10°C is placed on a reservoir at 100°C and allowed to come to thermal equilibrium. The process is then divided into two stages so that the block at 10°C is first brought to equilibrium with a reservoir at 55°C and then with a reservoir at 100°C. Calculate the entropy changes for the single-stage and double-stage processes. Why is there a difference between the two answers?

WORKED SOLUTIONS TO F31ST1 TUTORIAL WORK SET #3

Q1(a) Total number of possible poker hands: $\frac{52!}{47!5!}$ (the 5! in the denominator accounts for the possible permutations of 5 cards each giving rise to the same hand). Hence, total of 2,598,960 hands.

Q1(b) In the following I define a *face* as one of the 13 particular types of card (A, 2, 3,..., Q, K) in a *suit* (clubs, diamonds, spades, hearts).

- (i) Only 4 possible royal flush hands (one for each suit).
- (ii) A full house only uses two of the possible 13 faces. There are $\frac{13!}{1!!2!}$ combinations associated with this choice. Three of the cards in a full house are chosen from 4 suits, hence 4 (i.e. $\frac{4!}{3!!}$) combinations. The remaining two cards are also chosen from 4 suits, therefore $\frac{4!}{2!2!}$ combinations. In addition, the faces may be arranged in one of two ways (e.g. we could have 5¢, 5¢, 5♥, 3¢, 3¢ or 3¢, 3¢, 5♥, 5¢, 5¢). We get the total number of combinations by multiplying these values together, i.e.: $\frac{13!}{1!2!} \times \frac{4!}{3!1!} \times \frac{4!}{2!2!} \times 2$. Total number of full house hands = 3,744.
- (iii) A four-of-a-kind hand also involves only two of the 13 faces. Following the same reasoning as above, choose 2 faces from 13 in $\frac{13!}{11!2!}$ ways. Then, choose 4 cards from 4 suits in 1 way. The final card in the hand is also chosen from 4 suits and hence there are 4 ways of choosing this card. Again, the faces may be arranged in one of two ways. So, total number of four-of-a-kind hands = $\frac{13!}{11!2!} \times 1 \times 4 \times 2 = 624$.
- (iv) A hand of cards containing a pair will have a total of 4 different faces (eg for Q \clubsuit , Q \clubsuit , 5 \heartsuit , 7 \blacklozenge , 9 \bigstar the faces are Q, 5, 7, 9). There are thus $\frac{13!}{9!4!}$ ways of selecting the faces in the hand. Three of the faces in the hand may come from 4 suits (thus, 4 combinations for each card), the remaining face may also come from 4 suits (thus, 6 combinations). Finally, the pair can be any of the four faces in the hand. Hence, total number of combinations = $\frac{13!}{9!4!} \times 4^3 \times 6 \times 4 = 1,098,240$ separate hands. [3]
- (v) The total number of microstates associated with a 'junk' hand is simply the total number of possible hands minus the sum of the combinations given above = 2,598,960 (1,098,240 + 624 + 3744 + 4) = 1,496,348.

The most likely macrostate is obviously the 'junk' hand whereas the least likely macrostate is the royal flush because these are associated with the largest and smallest number of microstates respectively. **[1]** All *microstates* are equally probable.

Q1(c) The answer to this question was strongly hinted at in the footnote to Q1. We can't adopt Boltzmann's expression ($S = k \ln (W)$) to quantify the entropies of the various hands of cards because the distributions of the hands of cards are not described by Boltzmann statistics. That is, unlike the molecules of a gas, or the distribution of quanta of energy amongst harmonic oscillators (both covered in the lectures), the different microstates of the cards are not *accessible* via changes in the thermodynamics of the system.

Q2. Only (iii) and (iv) are possible answers. The total entropy of the Universe must at best remain constant (iii – a reversible process) or increase.

Q3.

Note that I have worked through questions 3(i) and 3(ii) in lecture 12. It will be interesting to see how many of the students can solve these problems in a tutorial.

3(i) The change in entropy of the block, ΔS_{Block} , is given by: $\Delta S_{Block} = \int_{373}^{283} \frac{dQ}{T}$

$$\Rightarrow \Delta S_{Block} = \int_{373}^{283} \frac{C}{T} dT = C \ln(\frac{283}{373})$$

$$\Rightarrow \Delta S_{Block} = -27.61 \text{ JK}^{-1}$$

The entropy gain of the lake is $\frac{C\Delta T}{T_{lake}} = 100 \times 90/283 = +31.80 \text{ JK}^{-1}$. (Lake acts as a thermal reservoir which is so large there's no change in its temperature).

Hence, net entropy change = $+4.19 \text{ JK}^{-1}$.

[Note: (a) temperatures must be in Kelvin; (b) block's temperature decreases \Rightarrow decrease in total number of available microstates \Rightarrow *negative* change in entropy (*for block*); (c) Heat capacity and not specific heat capacity was given so mass of block irrelevant.]

3(ii) The block is in the same state (at the same temperature) before and after the process. However, this is obviously an irreversible process. Although the temperature of the lake remains constant because it is a thermal reservoir, the kinetic energy of the block is transferred as heat energy into the lake. So there's a positive change of entropy for the lake:

$$\Rightarrow \Delta S_{lake} = \frac{mgh}{T_{lake}} = 1 \ge 9.81 \ge 10/283 = +0.35 \text{ JK}^{-1}$$

3(iii) Energy of the photon, *E*, is hc/λ where λ is 600 nm. Hence $E = 3.31 \times 10^{-19}$ J. So, change in entropy $= dQ/T = 3.31 \times 10^{-19}/283 = +1.17 \times 10^{-21}$ JK⁻¹. (Worthwhile noting here that although this seems to be a very small entropy change it still represents a very large change in the number of accessible microstates).

3(iv) The blocks when brought into contact will reach an equilibrium temperature of 328 K. The change in entropy for block 1 (whose temperature increases from 283 K to 328 K), $\Delta S_{block 1}$, is given by:

$$\Delta S_{block1} = \int_{283}^{328} \frac{C}{T} dT = C \ln(\frac{328}{283})$$
$$\Rightarrow \Delta S_{block1} = +14.76 \text{ JK}^{-1}$$

The change in entropy for block 2, $\Delta S_{block 2}$, is given by:

$$\Delta S_{block2} = \int_{373}^{328} \frac{C}{T} dT = C \ln(\frac{328}{373}) = -12.86 \text{ JK}^{-1}$$

So, *net* entropy change is $+ 1.9 \text{ JK}^{-1}$.

3(v) For the single stage heating of the block the changes in entropy of the block and the reservoir are:

$$\Delta S_{block} = C \ln(\frac{373}{283}) = +27.61 \text{ JK}^{-1}.$$

The change in entropy of the reservoir is $-\frac{\Delta Q}{T_{reservoir}} = \frac{C\Delta T}{T_{reservoir}} = -24.13 \text{ JK}^{-1}$

So, the total entropy change for the single stage process is +3.48 JK⁻¹.

The total entropy change for the two stage process is the sum of the entropy changes for the block and the reservoir:

$$\Delta S_{block} = C \left[\ln(\frac{328}{283}) + \ln(\frac{373}{328}) \right] = 27.56 \text{ JK}^{-1}$$
$$\Delta S_{RESERVOIR} = -C \left[\frac{45}{328} + \frac{45}{373} \right] = -25.77 \text{ JK}^{-1}$$

Hence net entropy change for two stage process is 1.79 JK⁻¹.

The two stage process has a **smaller** change in total entropy because it is closer to a *reversible* process.