

PAPER-3, 2022 Crib**SECTION A**

1.

(a)

Osmotic pressure describes the minimum pressure which needs to be applied to a solution to prevent the inward flow of its pure solvent across a semipermeable membrane. The physical origin arises from the entropy of mixing of solutes in solutions of different concentrations would want to drive for concentration equilibration. This formula applies when the solute concentration is sufficiently low that the solution can be treated as an ideal solution (i.e. no enthalpy of mixing is considered).

(b)

$$F_1 = \pi A = RTc_1A$$

$$c_1 = \frac{n}{A\left(\frac{L}{2}\right)} = \frac{F_1}{ART}$$

$$n = \frac{F_1L}{2RT}$$

[Examiner's comment: The diagram says 'top view', thus no effects of gravity need to be considered. Full mark is also given for answers in the form of $n = \frac{(F_1 - F_{bottom})L}{2RT}$, or $n = \frac{F_1LN_A}{2RT}$, where N_A is the Avogadro's constant.]

(c)

$$\begin{aligned} \text{Absolute Work done} &= \int_0^{\frac{L}{4}} F dx \\ &= A \int_0^{\frac{L}{4}} \pi dx = A \int_0^{\frac{L}{4}} RTc dx \\ &= ART \int_0^{\frac{L}{4}} \frac{n}{A\left(\frac{L}{2} - x\right)} dx = RT \int_0^{\frac{L}{4}} \frac{n}{\left(\frac{L}{2} - x\right)} dx \\ &\approx 0.693nRT \approx 0.347F_1L \end{aligned}$$

Assumptions: this would be the minimum work needed for separation, when F_{bottom} approaches 0. It omits the enthalpy of mixing, and assumes that separation process is extremely slow so that the system is always in equilibrium, and the force applied at the piston equals to the osmotic forces. The work deduced also ignores the hydrodynamic loss when pushing the liquid through the membrane. When the concentration of solute increases, the solution can no longer be considered as a 'dilute' system, but we still assume the ideal solution equation to work. So the work deduced will have to be the minimum work needed.

(d)

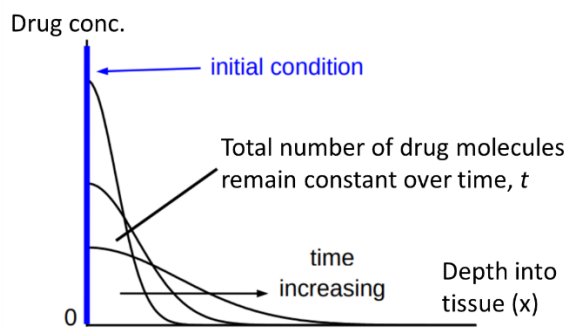
Rate will be dependant on the dissipative process of the fluid flow through the pores, thus membrane thickness, pore size & geometry, temperature, initial concentration of the solute.

[Examiner's comment: this was a new thermodynamics question which required students to apply the theory they learnt in the course into a practical scenario. This was the least popular question out of the paper with only one in five students attempted the question. Despite of the unfamiliarity, on average, the students could still achieve similar marks compared to other questions.]

2.

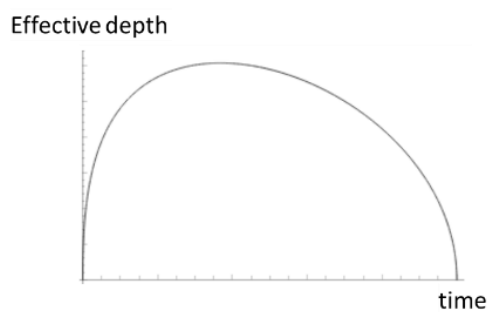
(a)

(i)



Assumptions: Instant drug release from the patch to skin; patch large, no-edge effects, thus the diffusion profile can be treated as a 1-D diffusion in the skin depth; skin as a homogeneous medium with depth $\gg \sqrt{Dt}$ for drug diffusion (where D is the diffusion constant of drug in skin, and t is time).

(ii)



[Examiner's comment: full mark is given for a graph shape approximate to the above.]

(iii)

Option- C

$$C_{\delta}(x, t) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{x^2}{2\sigma^2}\right) \text{ with } \sigma^2 = \langle x^2 \rangle = 2Dt \quad \text{for } x > 0$$

(iv)

$$c_{eff} = \frac{1}{\sqrt{2\pi}\sqrt{2Dt}}$$

$$t_{eff} = \frac{1}{4\pi D c_{eff}^2}$$

The patch is not effective when $c(x=0)$ reaches c_{eff} . The same assumptions need to be satisfied as shown in part-(i).

(b)

(i)

Under atmospheric pressure and normal room temperatures, the reaction between aluminium and oxygen has a negative free energy; but not gold.

(ii)

Graphite is highly conducting (due to delocalised electrons), is also cheap, robust, easily accessible, and high temperature-resistant. In addition, graphite lies in the positive side in the Galvanic series in e.g. ionic solutions. Thus, graphite is very inert.

(iii)

While the water is cooled below its thermodynamic freezing point, if the container is clean, and the cooling is slow, there will not be sufficient heterogeneous nucleation sites, or undercooling, to initiate the freezing process. When the water is poured onto a surface, heterogeneous nucleation occurs, which requires smaller undercooling, thus it can freeze quickly; and as fresh super-cooled water is added, it also freeze instantly.

[Examiner's comments: Part (a) of the question was designed to see whether knowledge learnt in the course can be translated to a different scenario. The statement of 'a thin patch with a finite amount of drug molecules' would set the initial and boundary conditions of the diffusion. Part (a) was answered well by about half of the cohort. For Part (b), three short questions were adapted from various thermodynamic considerations, and were answered well by most students.]

3.

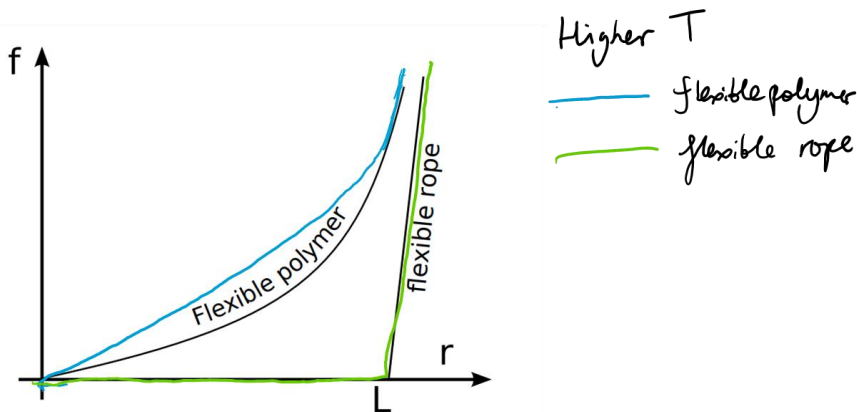
(a)

(i)

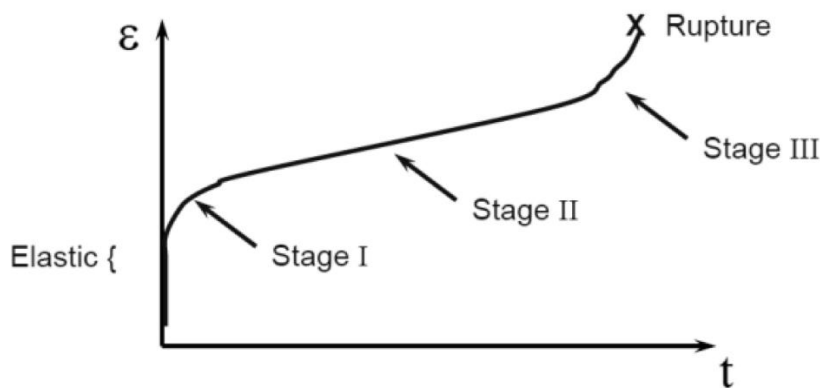
The flexible chain is a freely jointed chain, with a large number of n . Statistically, the monomers perform random walk, where such random walk is driven by thermal motion. There is no interaction between segments; very dilute chains like ideal gas; no external force applied to the chain. Thus, the mean end-to-end distance describes statistically, how far the starting points of the chain differ from the end points of the chain. The end-to-end chain distance thus follows the Gaussian statistics. the mean end-to-end distance is 0 considering a large number of configurations; and the mean square of end-to-end distance follows $\langle r^2 \rangle \propto na^2$.

(ii)

For a flexible polymer chain (no interaction between chain segments), at the limit of very small extensions, the polymer chain's stiffness is governed by entropic forces, thus it is expected to be linear (f vs. r) and have a low modulus. At the limit of very large extensions, the chains are fully unwinded, and becomes close to the conformation of a fully-extended rope, and thus the stiffness tends to that of the stretched rope. For the flexible rope, it is not subjected to entropic effects, so there is no stiffness at small extension until the rope is fully extended and we are stretching the rope (in the fully extended regime, f vs. r follows the Hooke's law with a linear relationship).



(b)



Stage I: Primary Creep

Stage II: Secondary Steady-state Creep

Stage III: Tertiary Creep

← dominates creep life

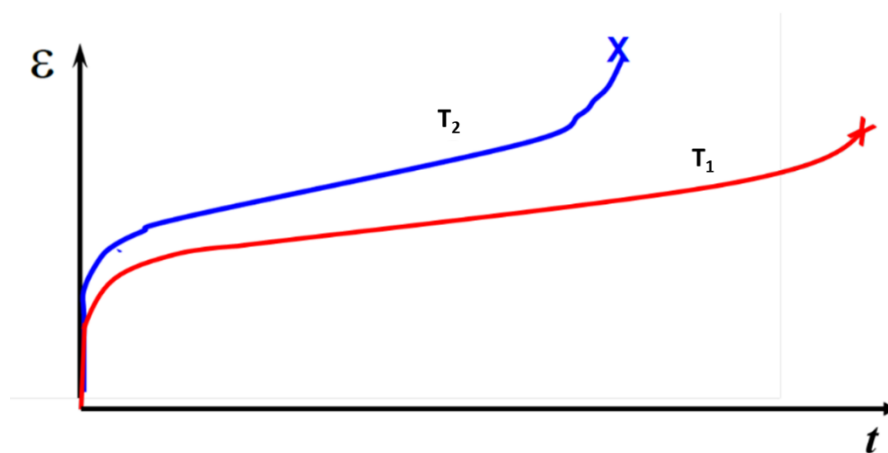
Three stages to the creep curve may be identified:

Stage I: Primary creep in which the creep resistance increases with strain leading to a decreasing creep strain rate. Little contribution to creep life.

Stage II: Secondary (Steady State) creep in which strain increases steadily with time (i.e. constant creep rate). This stage dominates creep life.

Stage III: Tertiary creep in which there is an accelerating creep rate due to the accumulating damage, which leads to creep rupture. Little contribution to creep life.

(ii)



The key differences include:

- Increased ϵ at the turning point between the elastic deformation and the Stage I creep.
- The stage II creep which dominates the creep life will proceed for a shorter period with a steeper gradient. This is due to the thermally activated nature of the creep deformation (i.e. $\epsilon \sim \exp(-Q/(RT))$).

(iii)

- 1) increase the grain size. This is because grain boundaries act as short-cut for faster diffusion. With larger grain size, larger diffusion distances, with lowered grain boundary area.
- 2) alloying. The solution hardening increases the resistance to dislocation motion.

[Examiner's comments: Part-(a) was a new question type derived from the course contents of polymer statistics. Part (a) was answered well by about half of the cohort. Part-(b) was a question on creep life, and was answered very well by most students.]

SECTION B

(a)

i)

It's steel – there are white areas and dark areas which on examination of the enlarged image are layer like in structure. The microstructures present therefore is likely to be a mixture of ferrite and pearlite. So we have primary ferrite grain microstructure containing ferrite phases which have formed and then when cooled through the eutectoid temperature pearlite has formed which consists of more ferrite and cementite phases.

ii)

The ferrite/pearlite microstructure can form through equilibrium processing, it is therefore reasonable to assume that this represents an equilibrium microstructure. There are no metastable phases present.

iii)

The relative proportions of the primary ferrite and pearlite tell us where on the eutectoid line to the left of the eutectoid point we were before the steel was cooled through the eutectoid reaction.

There is about 50% pearlite regions in this image – which puts us at about 0.4 wt% C. [As long as the reasoning is correctly explained – full marks this is not a test of estimating proportion]

iv)

This is “mild steel” – cheap and easily shaped which are very appropriate properties for an ornament. However mild steel is susceptible to corrosion which is likely to be a problem in an outdoors environment without some form of protection- paint or plastic dipping.

b)

i)

The hardenability of a steel is determined by CCR (critical cooling rate). Essentially this is the slowest we can cool and achieve 100% martensite. If we wish to subsequently temper the steel to obtain a specific hardness, we need therefore to be able to achieve 100% transformation. So steels with good hardenability will tend to have a small critical cooling rate.

ii)

As the C (carbon) content of steel is increased, the CCR increases. However we can also make alloy steel by incorporating other elements which tend to slow/inhibit diffusion in the steel.

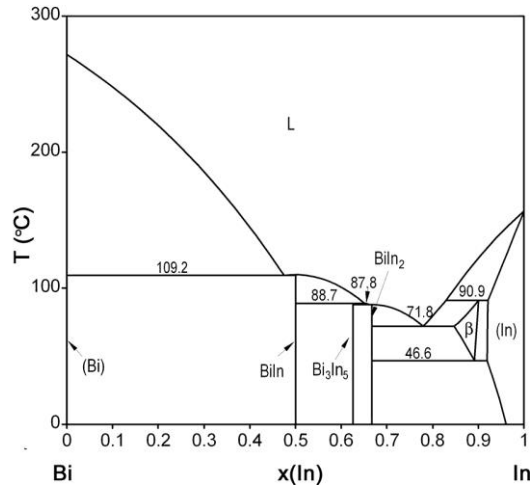
iii)

This requires that we consider the TTT diagram. Quenching misses the nose of the curve, so we have 100% austenite at that point (above Ms). At 625°C holding 40 minutes takes to ~30% conversion but all ferrite as we have not crossed the carbide line, at that point the balance is still austenite. After rapid quenching the remaining austenite becomes martensite as there is insufficient time to form anything else.

v)

To get to 100% bainite we need to quench past the first C-curve to 400°C in less than ~15 minutes and then hold for at least ~12 minutes.

5



i)

There are three – BiIn, Bi₃In₅ and BiIn₂ .

ii)

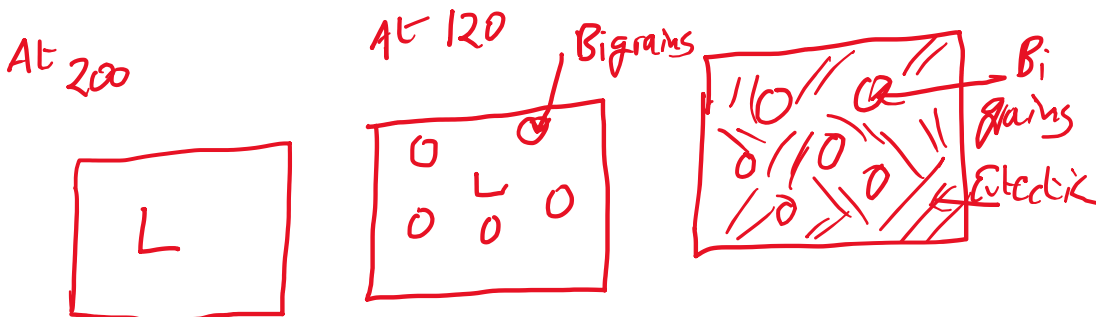
There are 6 reactions. – Eutectics at 109.2°C / 48%, 87.8°C / 65%, and 71.8°C / 78%. Peritectics at 88.7°C / 62% and 90.9°C / 90% and a eutectoid at 46.6°C / 89%

iii)

At A we have Bi (appears to be little solubility of In in Bi) so 0% at In. and liquid phase ~36% at% In. At B we have BiIn₂ and beta phase. The BiIn₂ is 66% at% In and the beta phase is ~88% at% In.

iv)

sketches reflect proportions using wt % scale for full marks



b)

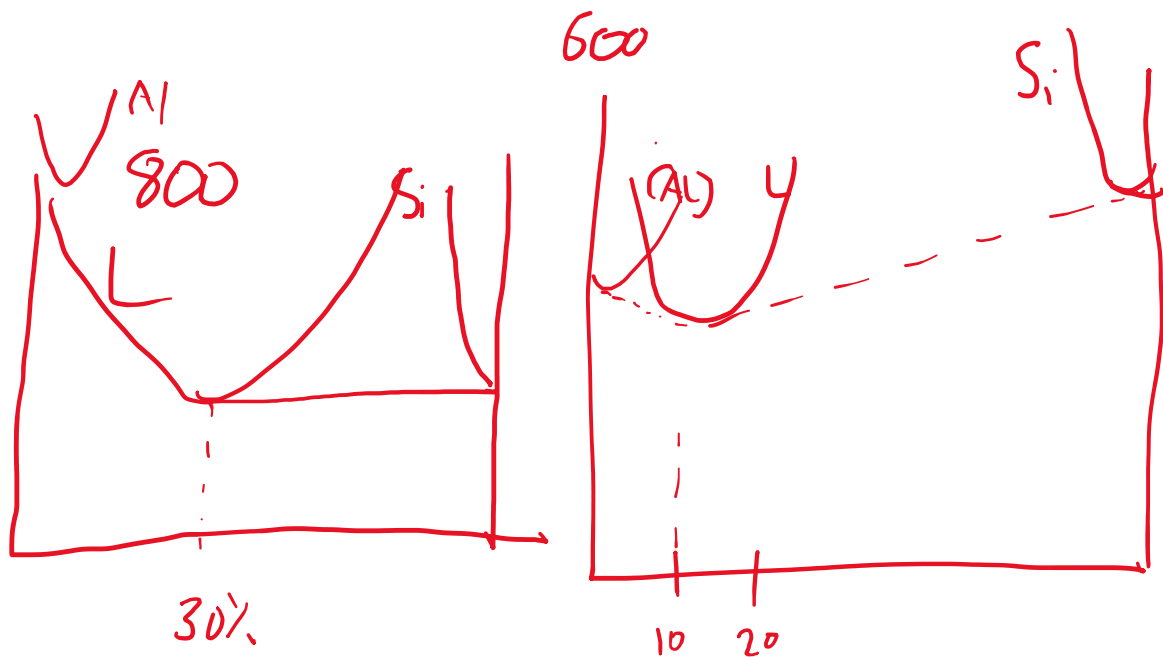
i)

Gibbs free energy is the amount of “extractable” energy that can do useful work for processes at constant pressure (which is what we have here). If we minimise Gibbs free energy the implication is that there is no more energy that can be extracted to do useful work and the system is stable. If we are not at a minimum in G further processes could occur.

ii)

If the surface energy at the interfaces between the phases is large – especially the case if there is a large lattice mismatch – there may be insufficient undercooling for nucleation to occur.

iii)



6.

a)

A material for deformation processing should, ideally, accommodate large strains without failing. A material exhibiting good plasticity is therefore required. High alloying elements may give too much hardening which inhibits this.

For casting we want good fluidity in the melt, so a melting point that is not too high. Casting alloys are often eutectics for this reason.

b)

Segregation – if we have a variation in properties this could lead to weakness at grain boundaries. Also segregation of impurities to the grain boundaries can also lead to reduced mechanical properties. We could:

Cool more slowly

Use an inoculant to get smaller grains

Insert an extra thermal processing step to homogenise

c)

To forge we need to reach the yield strength of the material by pressing uniaxially. As we press, the material will move outwards and this is opposed by friction (Tresca or Coloumb). The relative significance of this friction, compared to the force arising from the pressure applied to the rest of the piece, depends on the aspect ratio of the part for a given width.

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If there is no friction the aspect ratio is no longer relevant.

[Equation not required]

$$F = \int_{-w}^{+w} p(x) dx = 2wY \left(1 + \frac{mw}{4h} \right)$$

d)

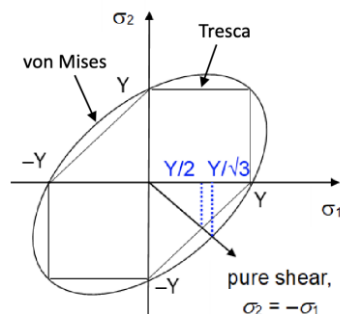
i)

We know that deformation will start at the surface so $r=R$. We can rearrange the equations to allow us to calculate the shear yield strength. This is $2 \times 200 / \pi (7.5e-3)^3$ which is 302 MPa

ii)

We now need to consider how shear and tensile yield strengths are related. We can choose one of two models, Tresca or van Mises with Tresca being more conservative.

Either model acceptable but Tresca easiest to remember and use.



Tensile yield strength is 604 MPa if we take Tresca.

iii)

We can start off by looking in data book for materials with a yield strength of this size. Alloy steel, for example, would satisfy the requirement, mild steel would not. We would also need a material that would not fail catastrophically in overload – so reasonable plastic region would be required. Selection should therefore be a ferreous material with good fracture toughness – so alloy steel not cast iron. This material is going to be subject to lots of stress cycles so a material that is fatigue resistant would be required.