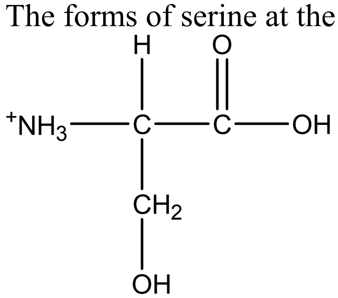
3.091 Fall Term 2002

Homework #12 with Solution Sketches

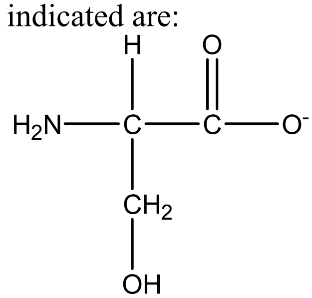
Biochemistry (to be tested)

BIO-1. Amino acids exist in aqueous solution as zwitterions because the carboxyl group ionizes to CO_2^- and the amino group at the other end is protonated and becomes positively charged to $-NH_3^+$. The result is a zwitterion, an ion that has both a positive and a negative charge.

BIO-4. The forms of serine at the pH indicated are:



at pH = 1



at pH = 13

BIO-5. Amino acids with nonpolar R groups will be able to form hydrophobic areas in the protein structure. Serine with a polar R group and lysine with a charged R group cannot contribute to the hydrophobic pocket. Responses (d) and (e).

BIO-6.

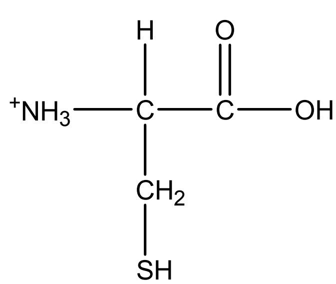
(a) Alanine	hydrophobic
(b) Glutamic acid	hydrophilic
(c) Arginine	hydrophilic
(d) Methionine	hydrophobic
(e) Threonine	hydrophilic

BIO-9. Since the pH lies below the isoelectric point of tyrosine, we would expect that on average, a tyrosine molecule would be positively charged.

BIO-11. The structure of **cysteine** at $pH = 7$ shows that the side group is protonated. So we must conclude that even though the pK_a is 8.33, the **sulfhydryl** (-SH) is acting as an acid.

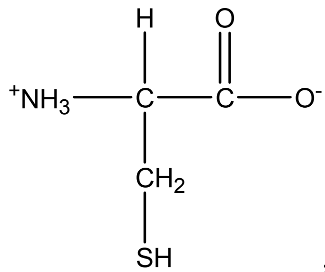
The **isoelectric point**, pI, is the pH at which the **zwitterion** is the dominant species.

Let's start with extreme acid conditions, $pH < 1.96$. Under these circumstances according to the **LeChatelier Principle** the amino acid will be fully protonated in an effort to try to consumer the proton excess in solution. The resulting structure of the amino acid is



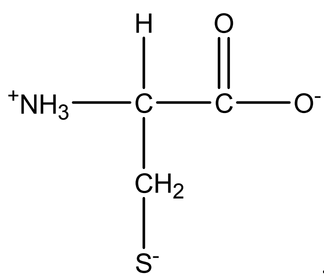
, which is net positive (**cationic**).

In slightly more alkaline solutions, $1.96 < pH < 8.33$, the carboxylic acid sheds its proton in order to neutralize OH^-. The resulting structure of the amino acid is



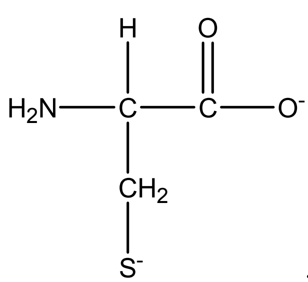
, which is the **zwitterion**. Hence we calculate the value of *pI* to be the average of 1.06 and 8.33 = 5.14.

Just to complete the analysis, consider still greater basicity, $8.33 < pH < 10.78$. Over this range of composition the resulting structure of the amino acid is



, which is net negative (**anionic**).

Finally, at extreme alkaline conditions, $pH > 10.78$, everything is deprotonated in an effort to neutralize the rising OH^- population. Over this range of composition the resulting structure of the amino acid is



, which is net negative and doubly charged (**anionic**).

Also worth mentioning, at neutral *pH*, reduced **sulfhydryls** on two different **cysteine** side groups can be **oxidized** to form **disulfide linkages**.

BIO-22. The following amino acids can form hydrogen bonds in the tertiary structure of a protein: arginine, asparagine, glutamine, histidine, lysine, serine, threonine, tyrosine.

BIO-25. (a) Increasing the temperature acts to rupture hydrogen bonding of both the secondary and tertiary structures.

(b) Changing the pH can disrupt the tertiary structure, removing hydrogen bonding sites, and if sufficiently severe, breaking the peptide bonds.

(c) Adding a detergent can disrupt the tertiary structure by interfering with both the hydrophilic and hydrophobic interactions.

(d) Addition of an oxidizing or reducing agent can seriously affect functional groups such as sulfides and alcohols.

(e) Addition of compounds such as urea serves to disrupt the hydrogen bonding in fixing the secondary and tertiary structure.

Phase Equilibria (to be tested on the Final)

1. For the binary system Cu-Ni the following data are available from cooling experiments:

T (°C)	melt composition (atomic % Ni)	composition of solid first formed on cooling (atomic % Ni)
1100	3	10
1180	20	37
1260	40	57
1340	60	73
1410	80	87

(a) From these data and information provided in the Periodic Table, construct the T/composition diagram.

(b) For the following temperatures and compositions, what are the phases present and what are their respective compositions?

T (°C)	Composition (atomic % Ni)
1120	15
1200	55
1300	60

2. Draw schematic phase diagrams for binary systems with (a) complete liquid and solid solubility, (b) complete liquid but zero solid solubility, and (c) complete liquid and limited solid solubility. (In your sketches label phase fields and give characteristic temperatures.)

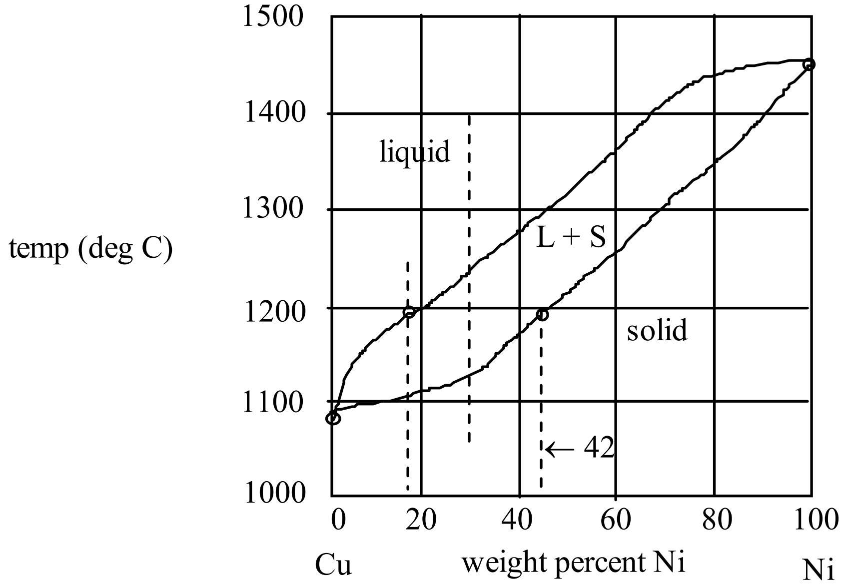
3. The Cu-Ni phase diagram is given on the next page. Refer to it in answering the following questions.

For a sample of composition 70 wt. % Cu and 30 wt. % Ni held at 1200°C, determine the following:

(a) The composition of the solid phase in equilibrium with the liquid.

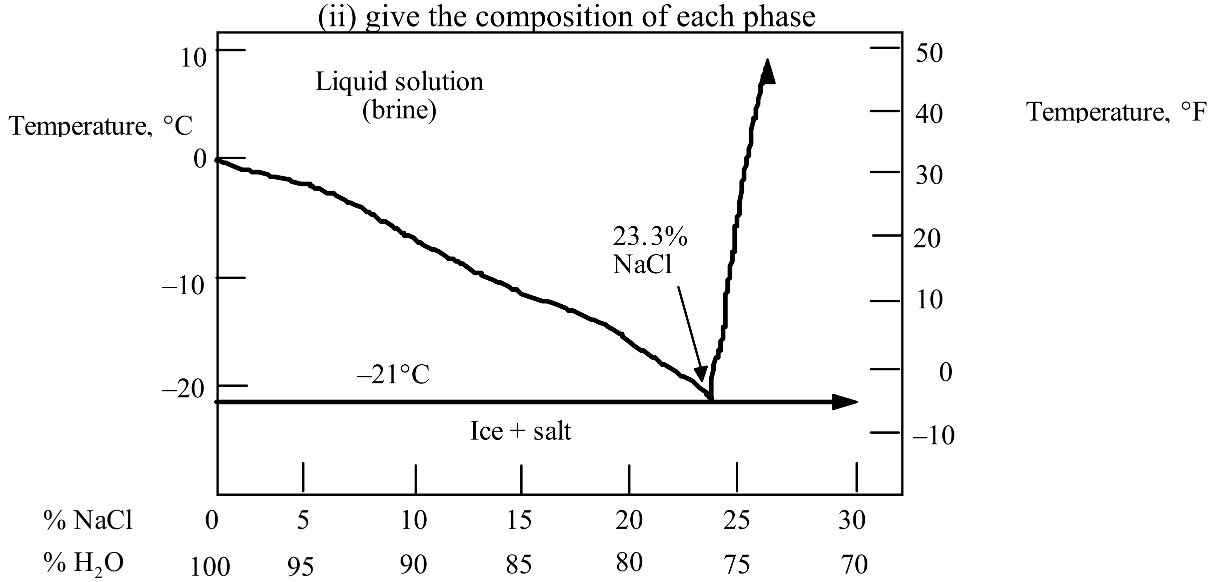
(b) The composition of the liquid in equilibrium with the solid.

(c) The weight percent of solid phase at this temperature.



4. (a) At each of the following coordinates on the binary phase diagram of NaCl – H_2O (see next page) at 1 atmosphere pressure, (i) identify the stable phases,
(ii) give their compositions, and
(iii) calculate their relative proportions:
(1) 10% NaCl, 0°C
(2) 10% NaCl, –10°C
(3) 10% NaCl, –25°C

(b) For a solution of 23.3% NaCl in H_2O at –21°C,
(i) identify the stable phases present, and
(ii) give the composition of each phase



5. (a) For each of the following Ag-Cu alloys state all phases present at the specified compositions and temperatures. Phase diagram givern below.

(i) c = 20 atomic per cent Cu, T = 900°C
(ii) c = 20 atomic per cent Cu, T = 800°C
(iii) c = 20 atomic per cent Cu, T = 700°C
(iv) c = 5 atomic per cent Cu, T = 700°C
(v) c = 80 atomic per cent Cu, T = 800°C

(b) For the Ag-Cu alloy, c = 70 atomic per cent copper, calculate the relative amounts of all phases present at T = 600°C.

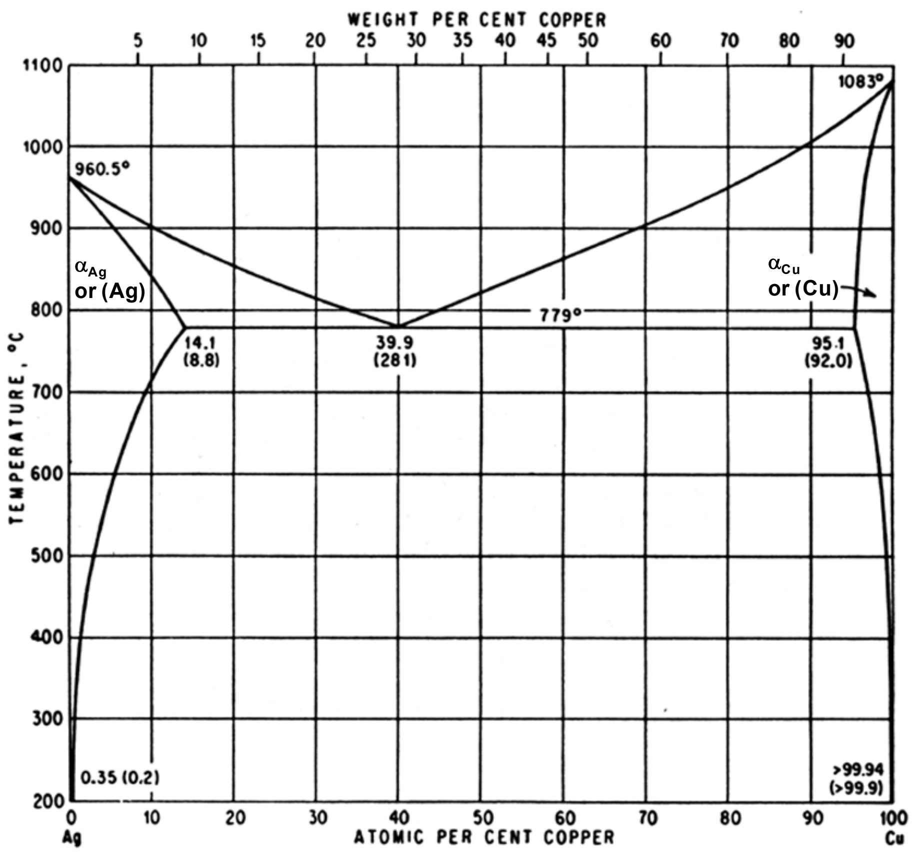


Fig. 11. Ag-Cu

6. (a) For each of the following Pb-Sn alloys state all phases present at the specified compositions and temperatures. Phase diagram given on the following page.

(i) c = 10 atomic per cent Pb, T = 300°C
(ii) c = 10 atomic per cent Pb, T = 200°C
(iii) c = 10 atomic per cent Pb, T = 100°C
(iv) c = 90 atomic per cent Pb, T = 200°C
(v) c = 60 atomic per cent Pb, T = 200°C

(b) For the Pb-Sn alloy, c = 60 atomic per cent lead, calculate the relative amounts of all phases present at T = 200°C.

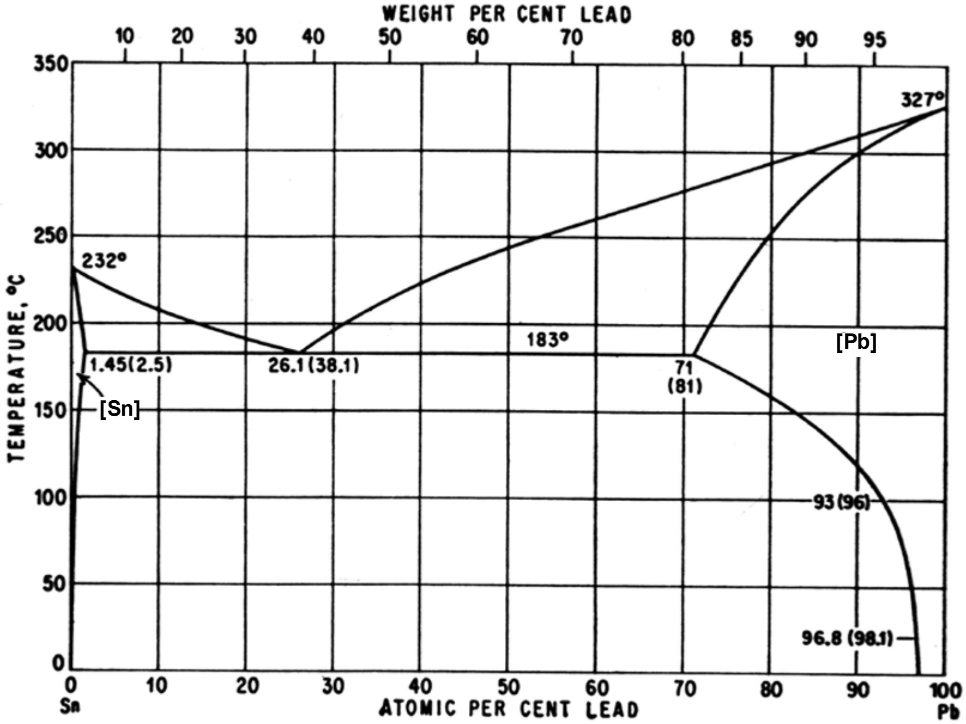


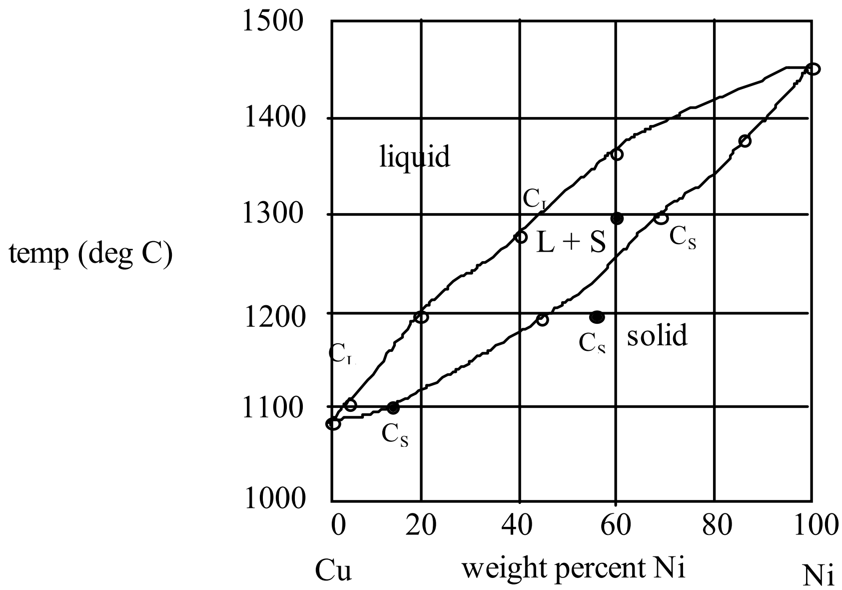
Fig. 601. Pb-Sn

7. Given the triple point of copper (Cu) and data provided in the Periodic Table, sketch a reasonable P/T equilibrium phase diagram for copper.

Triple point: $T_T = 1080°C$

$P_T = 6.1 \times 10^{-6}$ atm

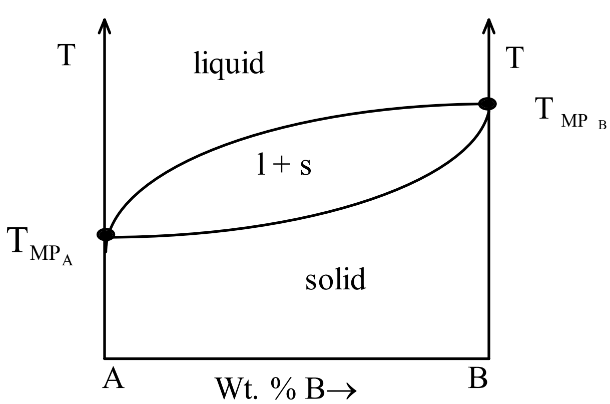
1. (a)



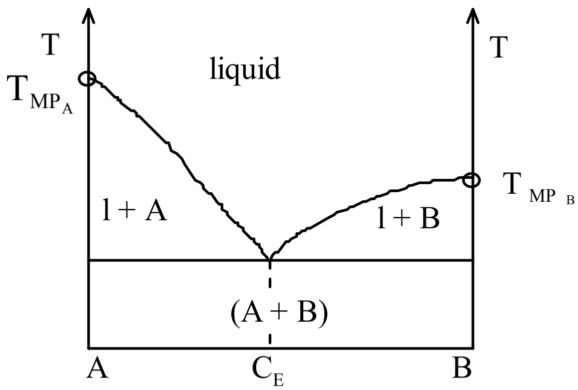
(b)

T (°C)	Composition (atomic % Ni)	Phase	Composition (atomic % Ni)
1120	15	Solid Liquid	17 07
1200	55	Solid	55
1300	60	Solid Liquid	68 45

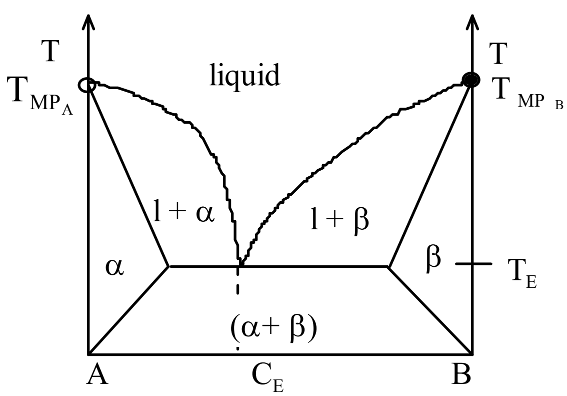
2. (a)



(b)



(c)

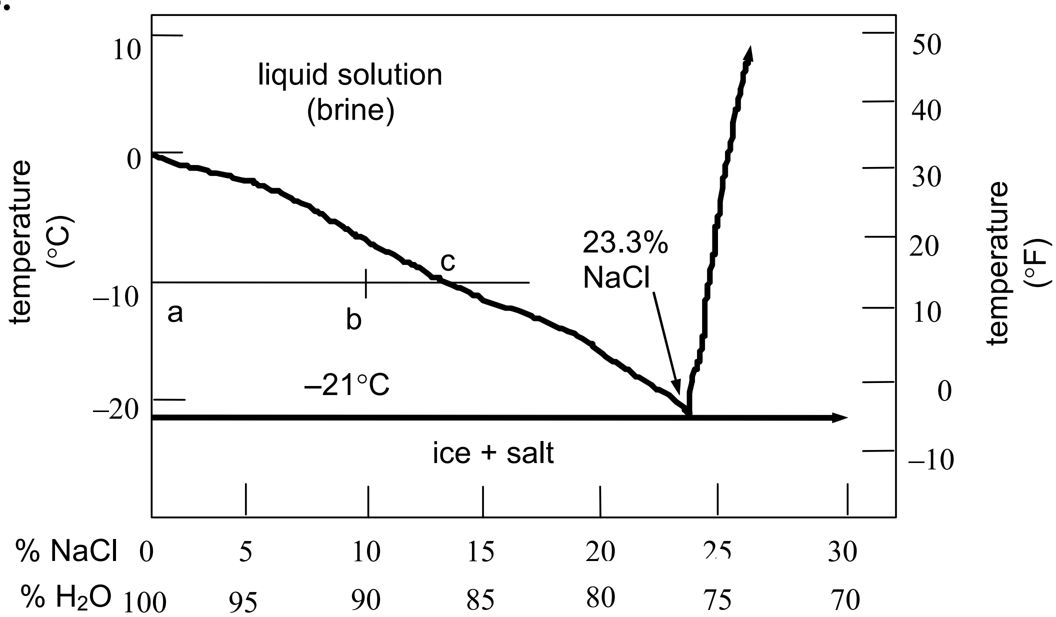


3. (a) C_{solid}: 42 wt. % Ni; 58 wt. % Cu

(b) C_{liquid}: 19 wt. % Ni; 81 wt. % Cu

(c) solid wt. % = $\frac{30-19}{42-19} \times 100 = 48$ wt. %

4.



(a) (1) (i) brine — all liquid

(ii) 10% NaCl in H_2O

(iii) 100% liquid

(2) (i) solid ice (H_2O) + liquid brine

(ii) solid — pure H_2O

liquid ≅ 15% NaCl in liquid H_2O

(iii) use lever rule:

$$\% \text{ ice} = \frac{bc}{ac} \times 100 \cong 30\%$$

$$\% \text{ brine} = \frac{ab}{ac} \times 100 \cong 70\%$$

(3) (i) pure ice (H_2O) + pure salt

(ii) ice phase = 100% H_2O; salt phase = 100% NaCl

(iii) 10% NaCl; 90% H_2O

(b) (i) brine (liquid) + 2 solids: NaCl (s) + H_2O (s)

(ii) 23.3% NaCl in water
pure NaCl (solid)
pure H_2O (solid)

5. (a) (i) all liquid

(ii) liquid + Ag-rich solution solution of Ag-Cu (denoted α Ag)

(iii) Ag-rich solid solution of Ag-Cu (denoted α Ag)
+ Cu-rich solution solution of Ag-Cu (denoted α Cu)

(iv) Ag-rich solid solution of Ag-Cu (denoted α Ag)

(v) liquid + Cu-rich solution solution of Ag-Cu (denoted α Cu)

(b) $\% \text{ (Cu-rich solution solution of Ag-Cu)} = \frac{70 - 5}{98 - 5} \times 100\% = 70\%$

$\% \text{ (Ag-rich solution solution of Ag-Cu)} = \frac{98 - 70}{98 - 5} \times 100\% = 30\%$

6. (a) (i) all liquid

(ii) liquid + Sn-rich solution of Sn-Pb

(iii) (Sn-rich solid solution of Sn-Pb)
+ (Pb-rich solid solution of Sn-Pb)

(iv) Pb-rich solid solution of Sn-Pb

(v) liquid + (Pb-rich solid solution of Sn-B)

(b) $\% \text{ liquid} = \frac{73 - 60}{73 - 31} \times 100\% = 31\%$

$\% \text{ (Pb-rich solid solution of Sn-Pb)} = \frac{73 - 60}{73 - 31} \times 100\% = 31\%$

7.