3. Binary electrodes under equilibrium or near-equilibrium (Huggins, ch. 3)

1. Binary phase diagrams
2. A real example, the lithium: antimony system
3. Another example, the lithium: bismuth system
4. Temperature dependence of the potential
5. Application to oxides and similar materials
6. Ellingham diagrams
7. Liquid binary electrodes

1. Binary Phase Diagrams

-Phase diagrams are figures that graphically represent the equilibrium state of a chemical system.

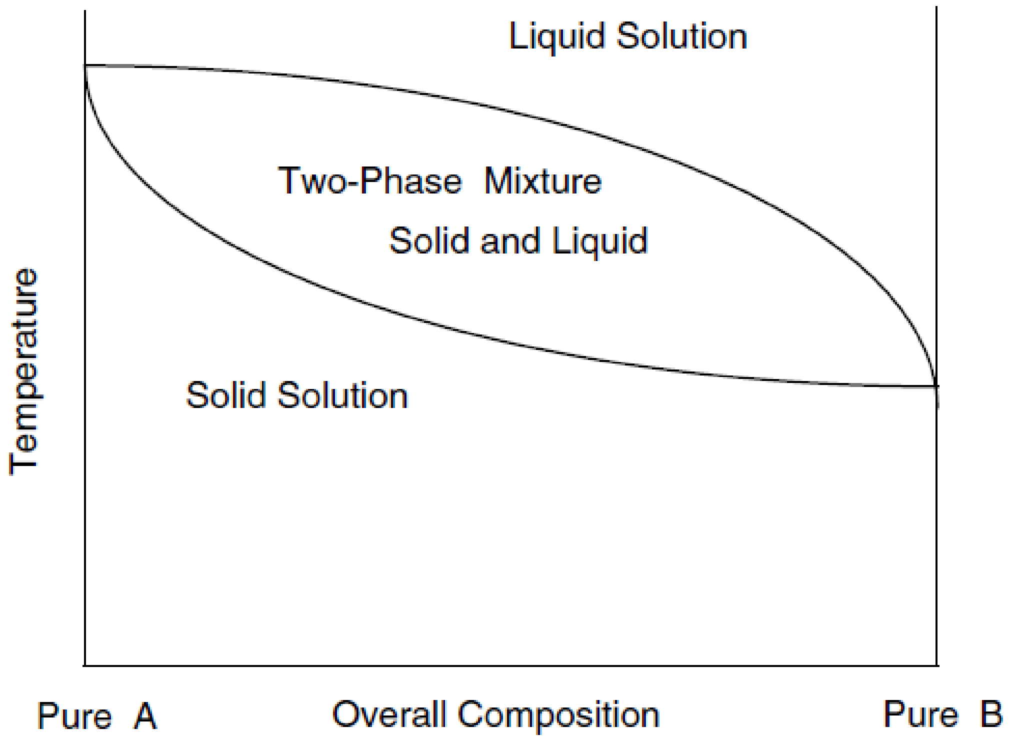

Fig. 3.1 Schematic phase diagram of binary system with complete miscibility in both the liquid and solid phases

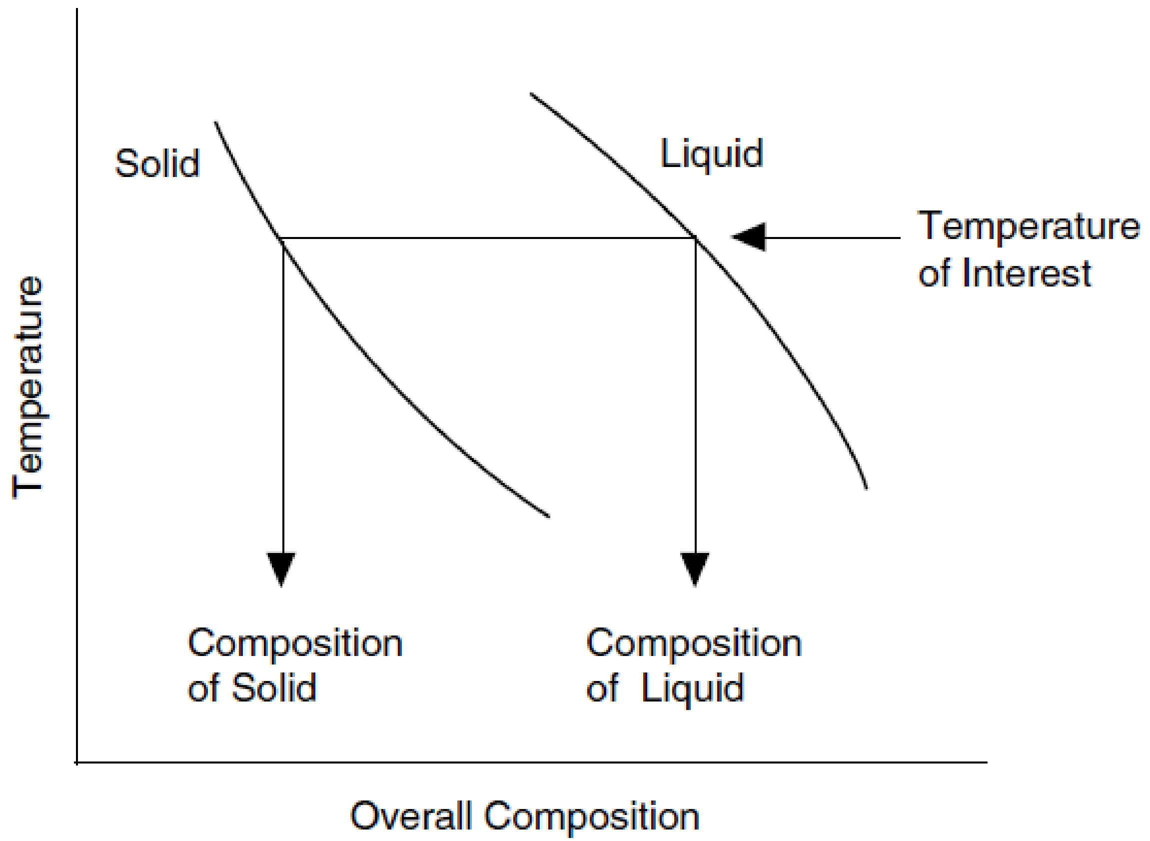

Fig. 3.2 Compositions of liquid and solid phases in equilibrium with each other at a particular temperature between the melting points of the two elements

1.1 The Lever Rule

The condition for balance is the ratio of the lengths L_2 and L_1 be equal to the ratio of the masses M_1 and M_2. i.e.

$$M_1/M_2 = L_2/L_1$$

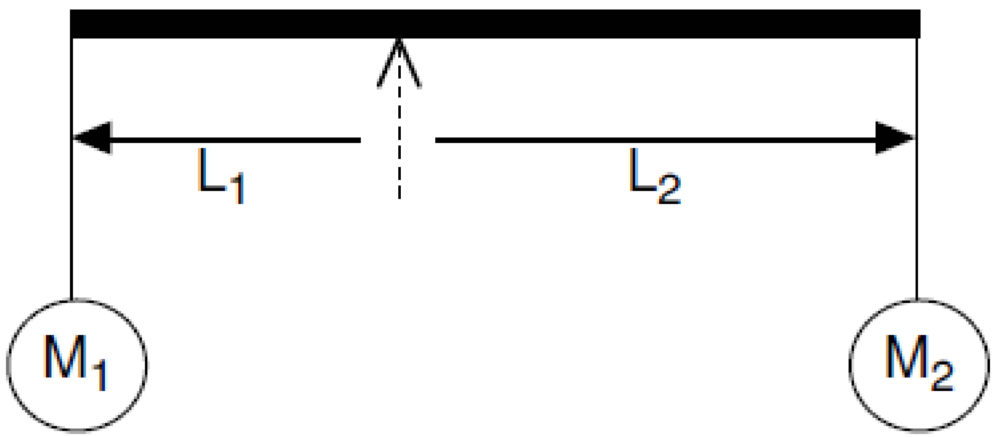

Fig. 3.3 Mechanical lever analog

$$Q_1/Q_2 = L_2/L_1$$

Q_1 and Q_2 represent the amounts of phases 1 and 2

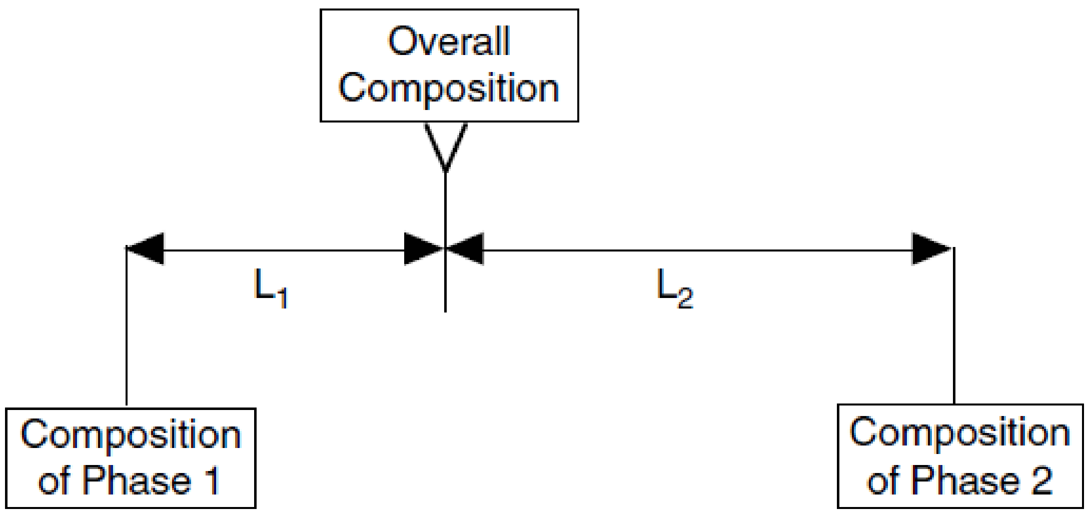

Fig. 3.4 Application of the lever rule to compositions in a two-phase region of a binary phase diagram

1.2 Examples of Binary Phase Diagrams

-four one-phase regions. The solid phases are designated as phases α, β and γ. Liquid phase at higher T. Two-phase regions

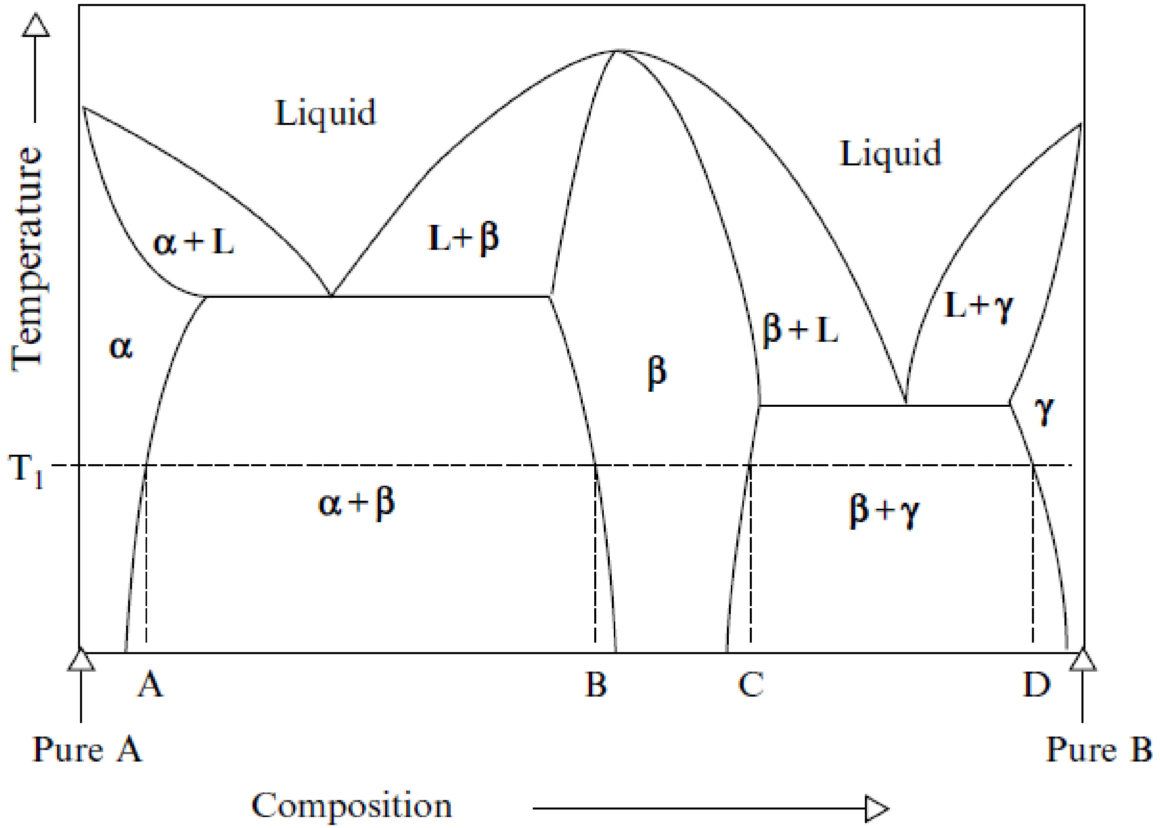

Fig. 3.5 Schematic binary phase diagram with an intermediate phase β, and solid solubility in terminal phases α and γ

-Gibbs Phase Rule:

Single-phase regions in a binary system: F = C – P + 2 = 2 – 1 + 2 = 3 → electrical potential varies with composition within single-phase regions (at const T & P)

It is composition-independent when two phases are present in a binary system (F = 2 – 2 + 2 = 2)

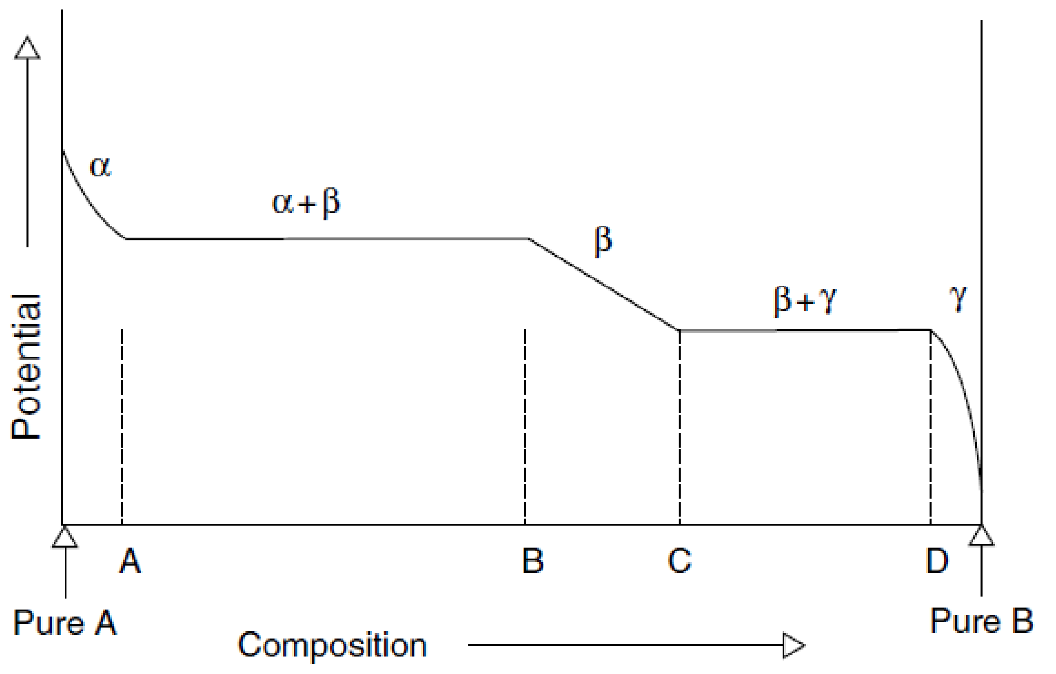

Fig. 3.6 Schematic variation of electrical potential with composition across the binary phase diagram shown in Fig. 3.5

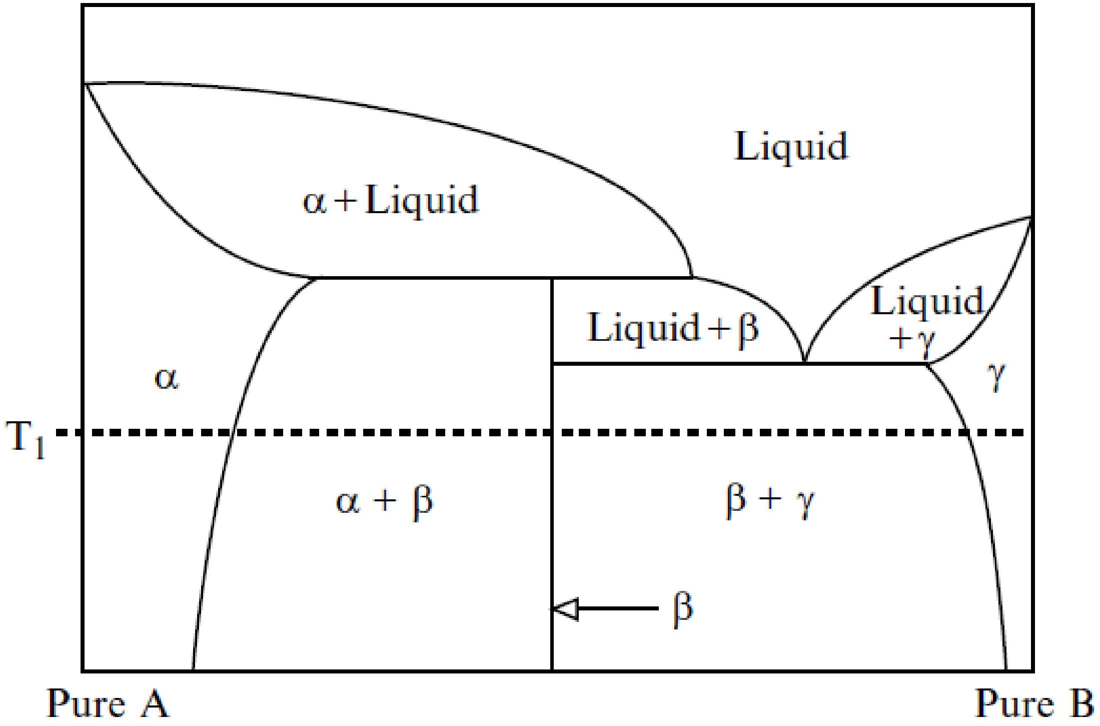

Fig. 3.7 Hhypothetical binary phase diagram in which the intermediate β phase has a small range of composition

-Line phase (β): quite narrow

-Potential drops abruptly due to line phase (β): quite narrow

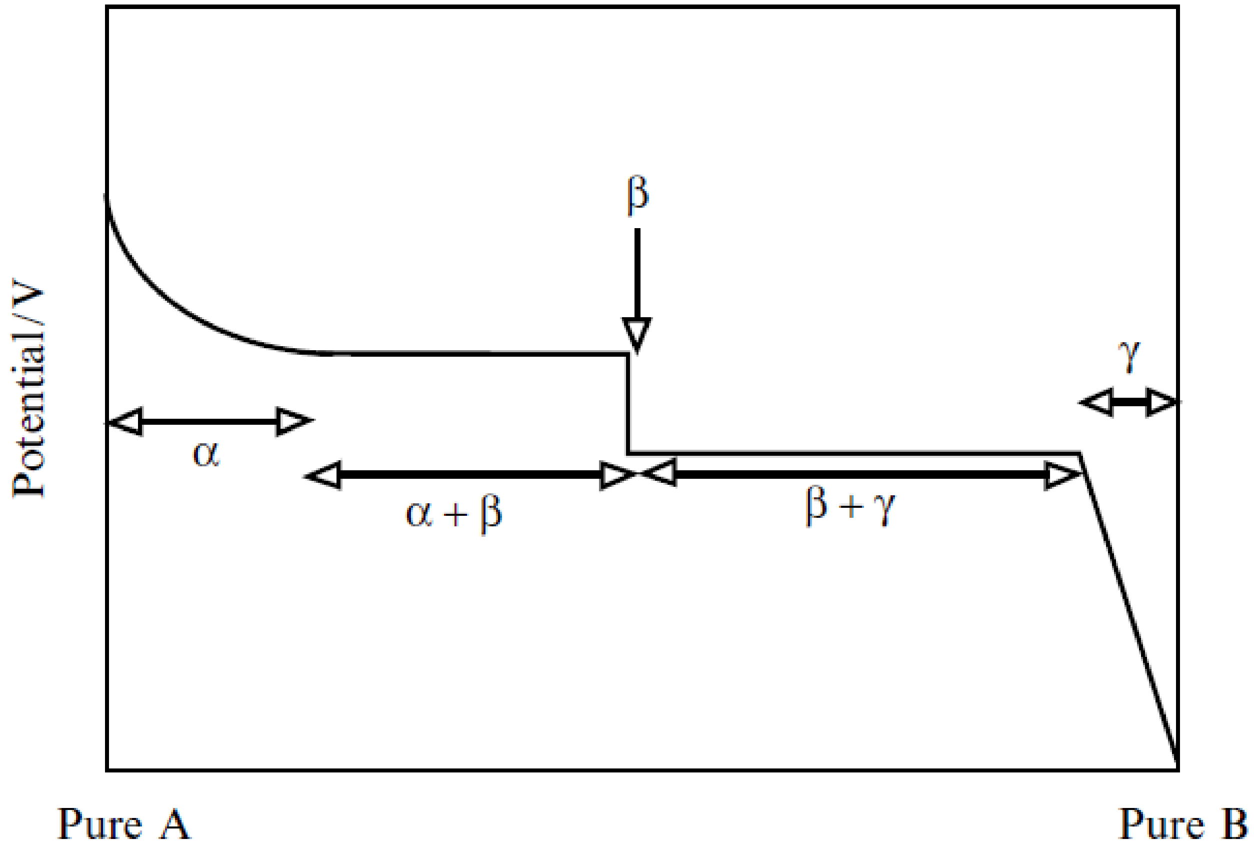

Fig. 3.8 Schematic variation of electrical potential with composition across the binary phase diagram shown in Fig. 3.7

2. A real example, the lithium: antimony system

<615℃, two intermediate phase: Li_2Sb, Li_3Sb

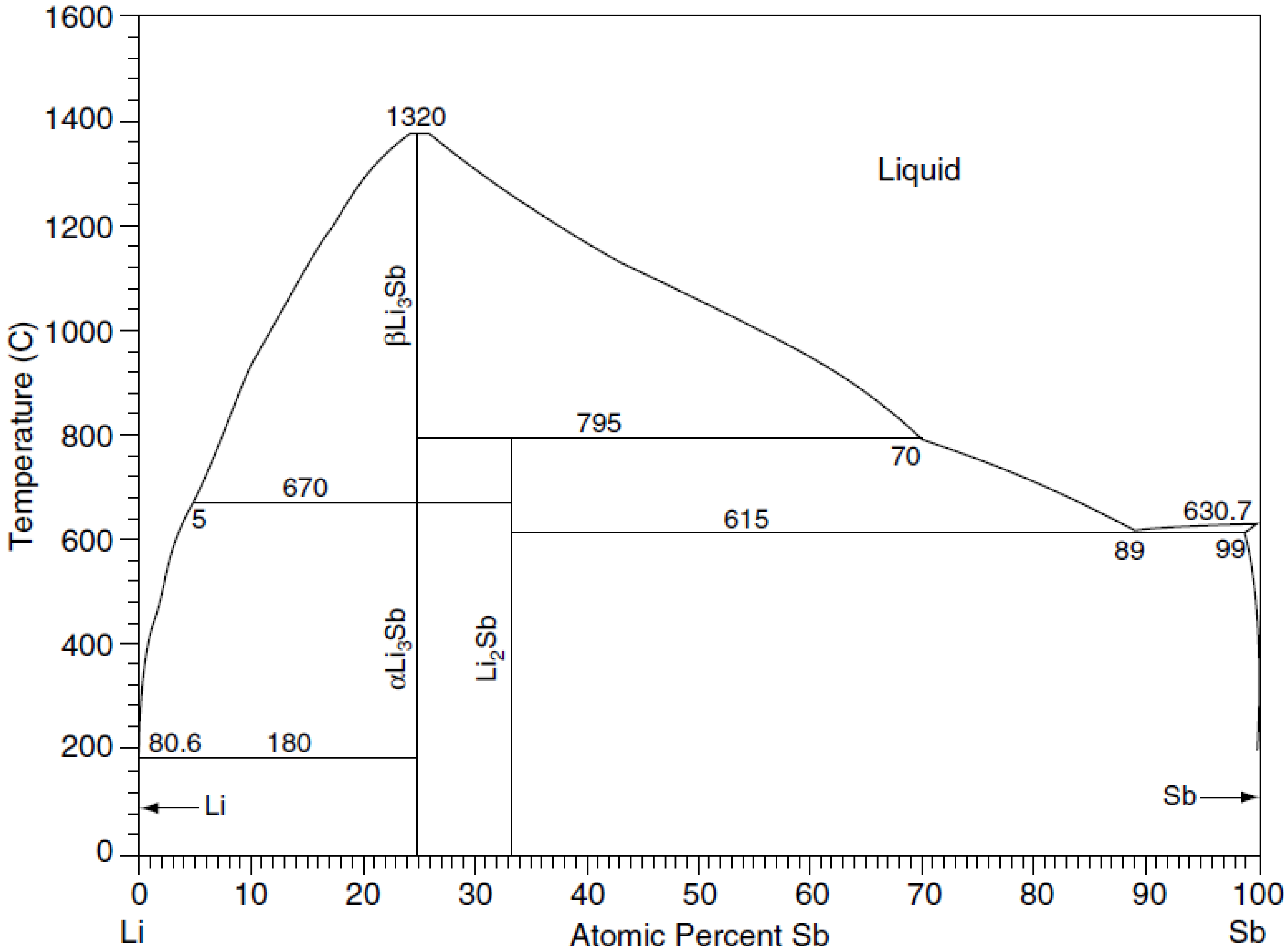

Fig. 3.9 Lithium–antimony phase diagram

In pure Sb, addition of Li,

$$2Li + Sb = Li_2Sb$$

On further addition of lithium,

$$Li + Li_2Sb = Li_3Sb$$

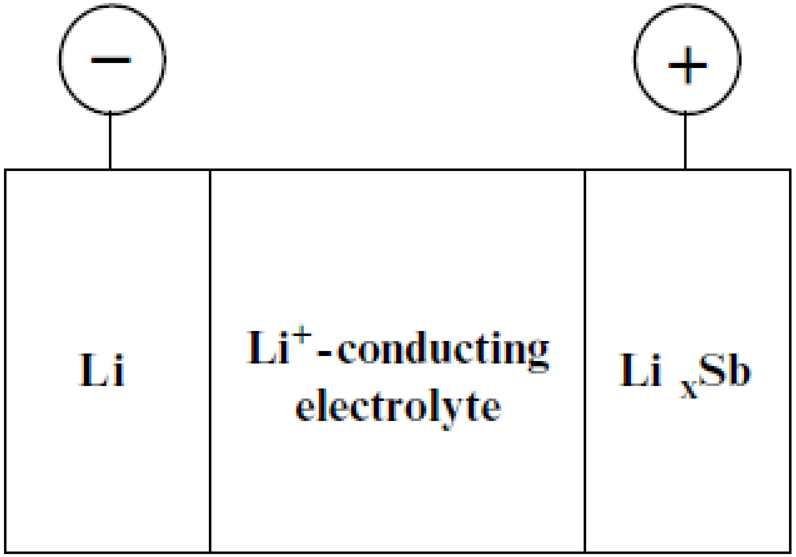

Fig. 3.10 Schematic drawing of electrochemical cell to study the Li–Sb system

Coulometric titration at 360℃

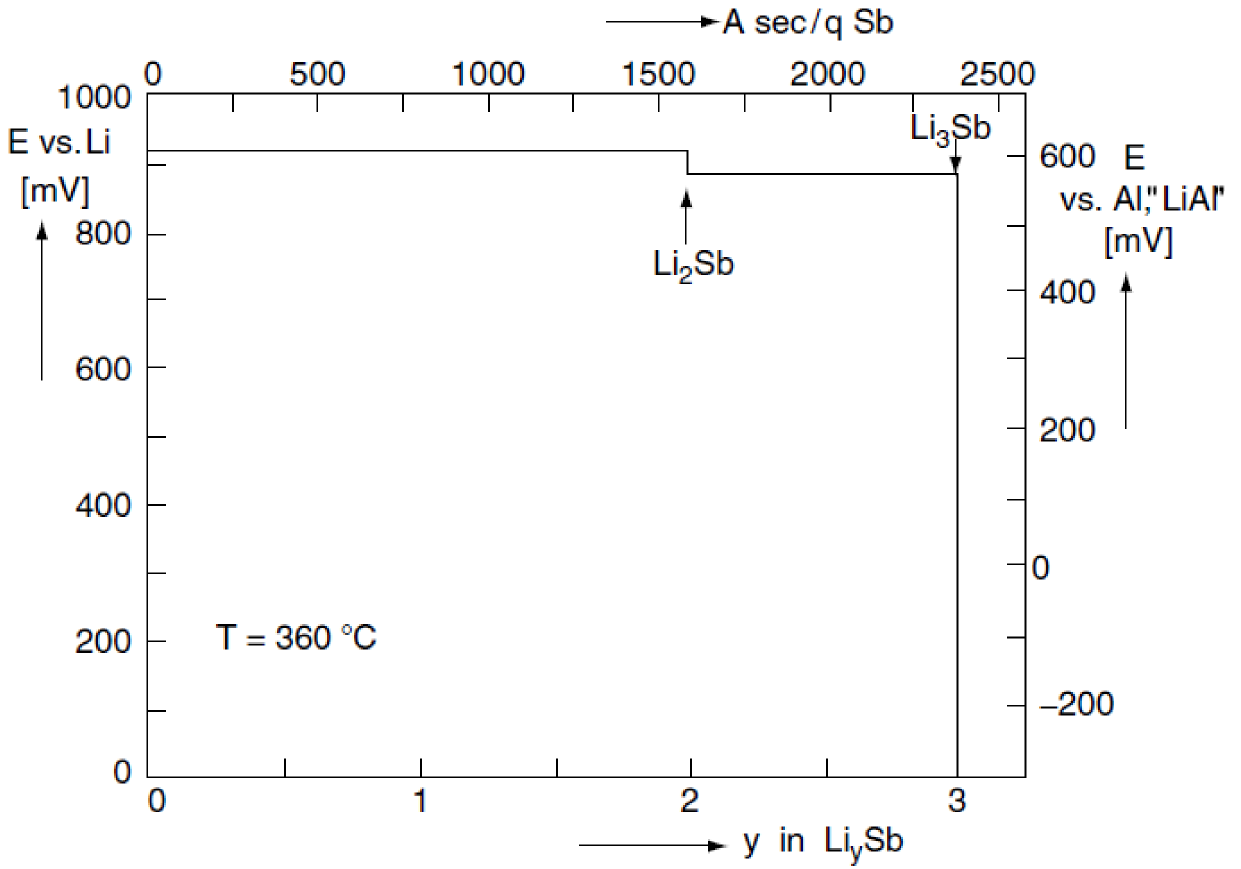

Fig. 3.11 Results from a coulometric titration experiment on the Li–Sb system at 360°C [3]

Potentials of the two plateaus are calculated from thermodynamic data on the standard Gibbs free energies of formation of the two phases, Li_2Sb and Li_3Sb. (−176.0 kJ/mol and −260.1 kJ/mol, respectively, at 360℃)

1st plateau: standard Gibbs free energy change(ΔG_r^o) = formation of phase Li_2Sb, $\Delta G_f^o(Li_2Sb)$

$$E - E^o = -\Delta G_r^o / 2F$$

where E^o is the potential of pure Li. This was 912mV in the experiment

HW#6

2nd plateau:

$$\Delta G_r^\circ = \Delta G_f^\circ(Li_3Sb) - \Delta G_f^\circ(Li_2Sb)$$

$$E - E^o = -\Delta G_r^o / F$$

This was 871mV in the experiment

-Maximum theoretical energy → total energy A + B
-Energy(J) = Voltage (V) x Capacity(C)
-total energy can be converted into specific energy (kJ/kg)

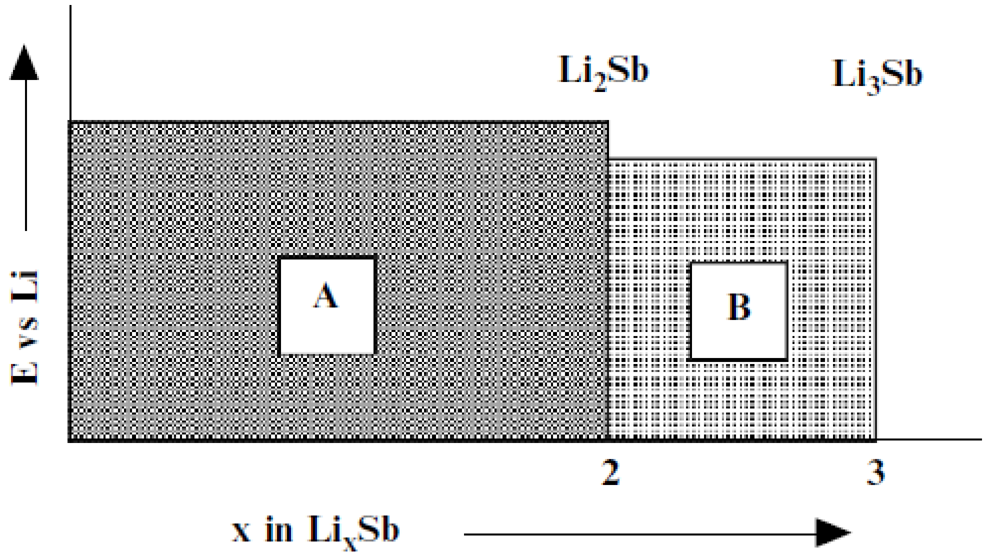

Fig. 3.12 Relation between energy stored and the titration curve in the Li–Sb system

1^{st} plateau, maximum theoretical specific energy (MTSE)
→ 1,298 kJ/kg = 360Wh/kg

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2^{nd} plateau, MTSE = 589 kJ/kg = 164Wh/kg

3. Another example, Li-Bi system

Bismuth at 360℃

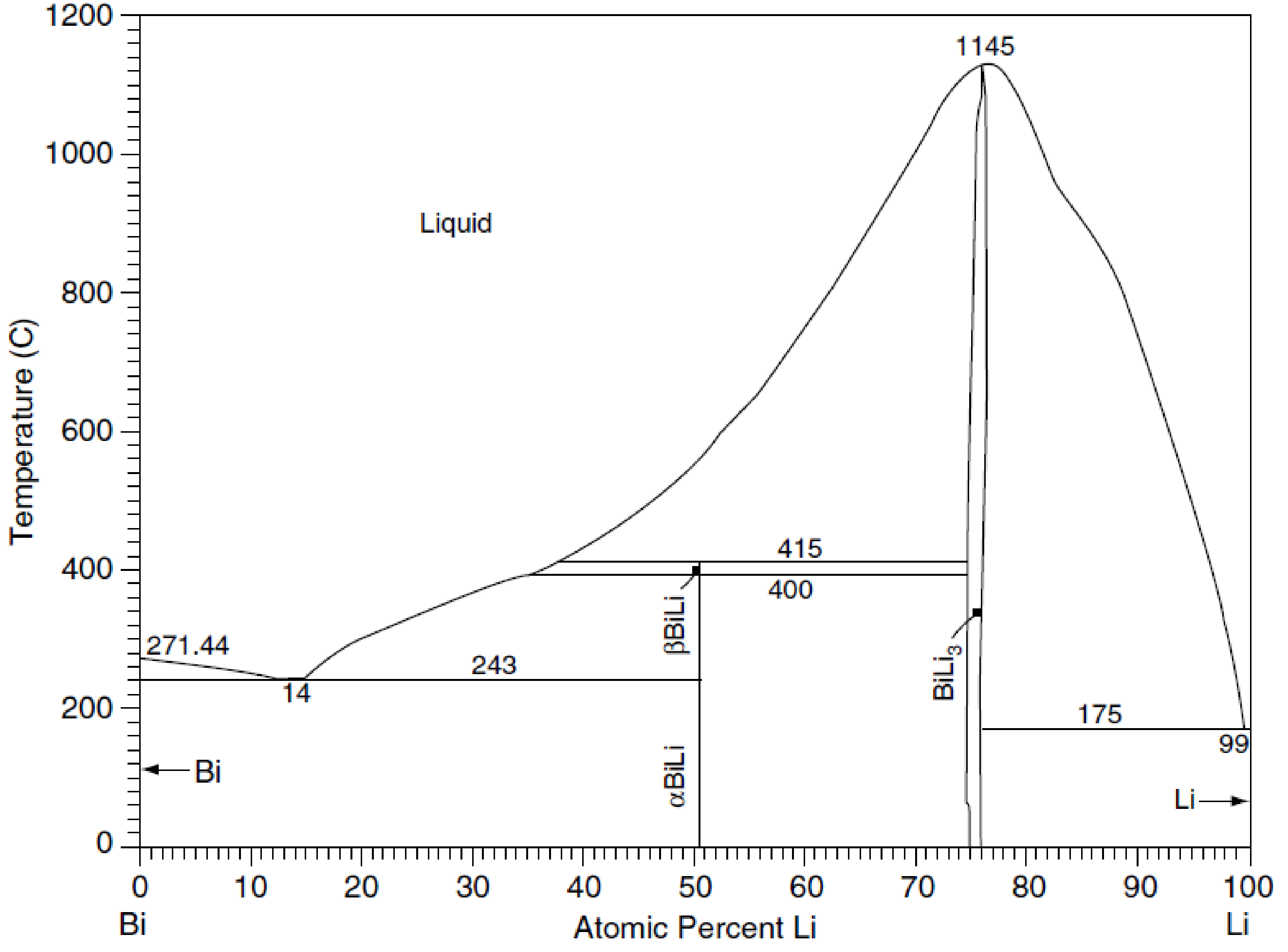

Fig. 3.13 The lithium–bismuth binary phase diagram

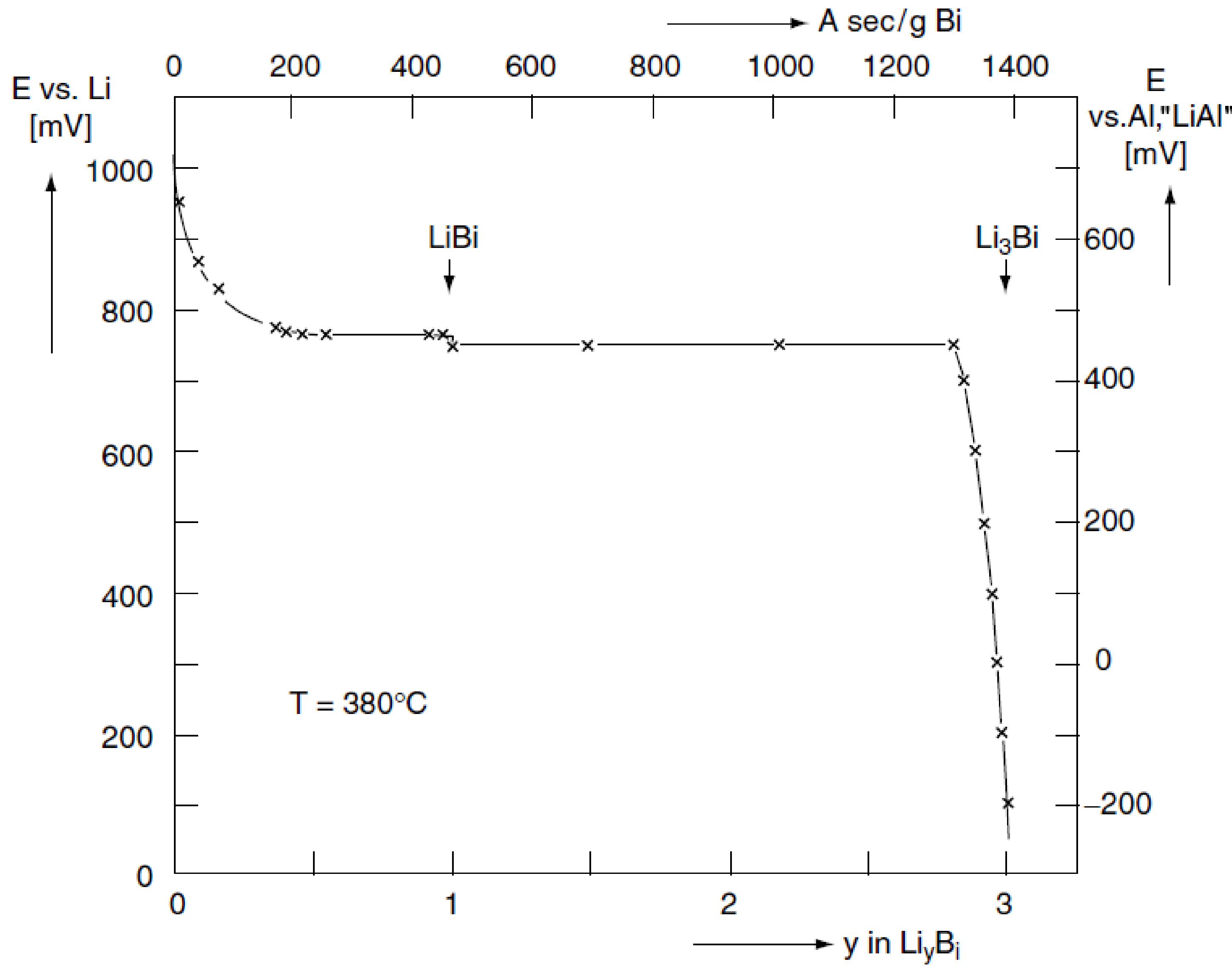

Fig. 3.14 Results from a coulometric titration experiment on the Li–Bi system at 360°C [3]

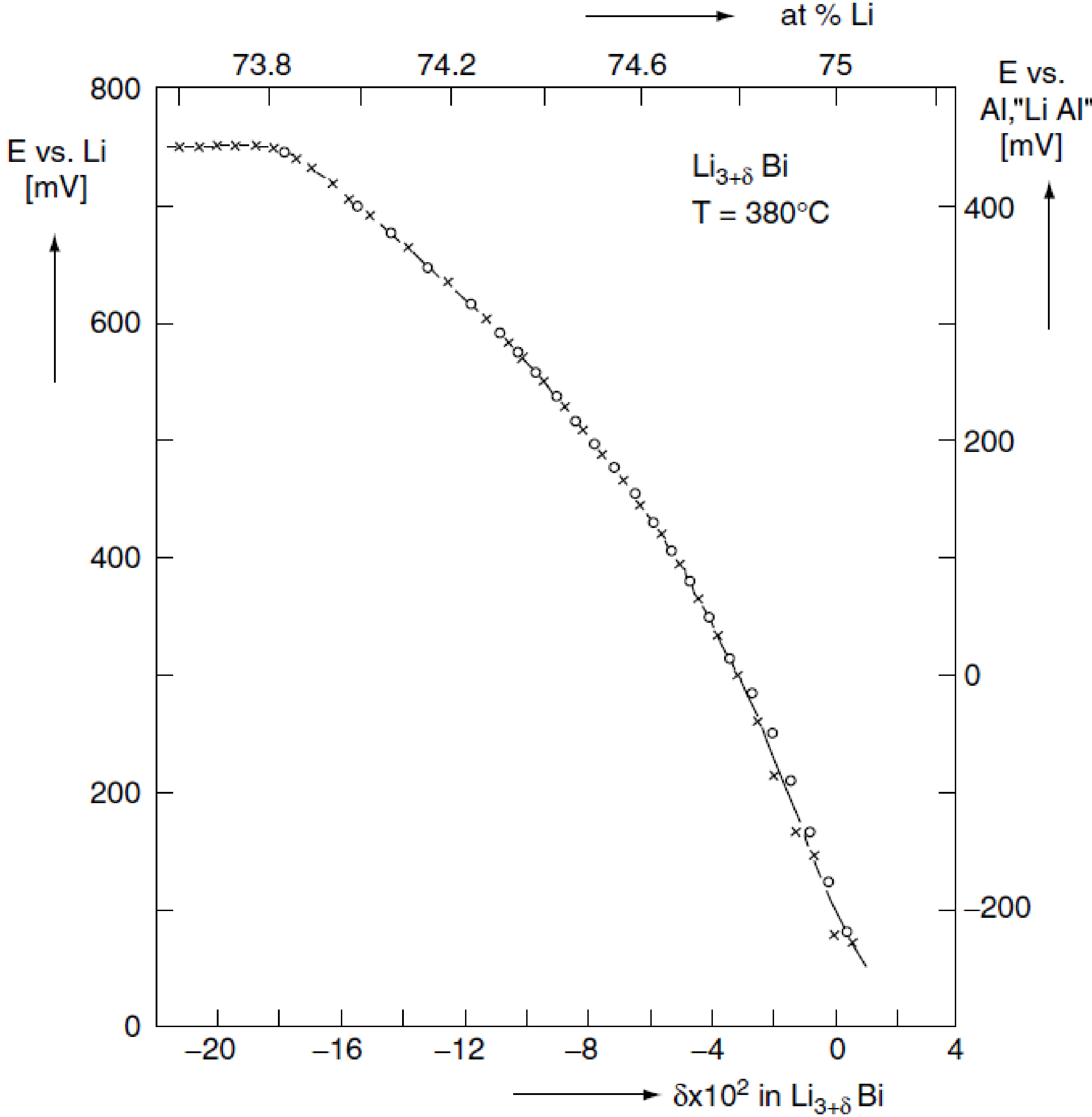

Fig. 3.15 Coulometric titration measurements within the composition range of the phase "Li_3Bi"

4. Temperature dependence of the potential

In the Li-Sb system,

$$2Li+Sb = Li_2Sb$$
$$Li+Li_2Sb = Li_3Sb$$

In the Li–Bi case, $Li+Bi = LiBi$

$$2Li+LiBi = Li_3Bi$$

-the temperature dependence of the plateau potentials is different. There is a change in the slope at the eutectic melting point (243◦C), and the data for the two plateaus converge at about 420◦C, which corresponds to the fact that the LiBi phase is no longer stable above that temperature. At higher temperatures there is only a single reaction; $3Li+Bi = Li_3Bi$

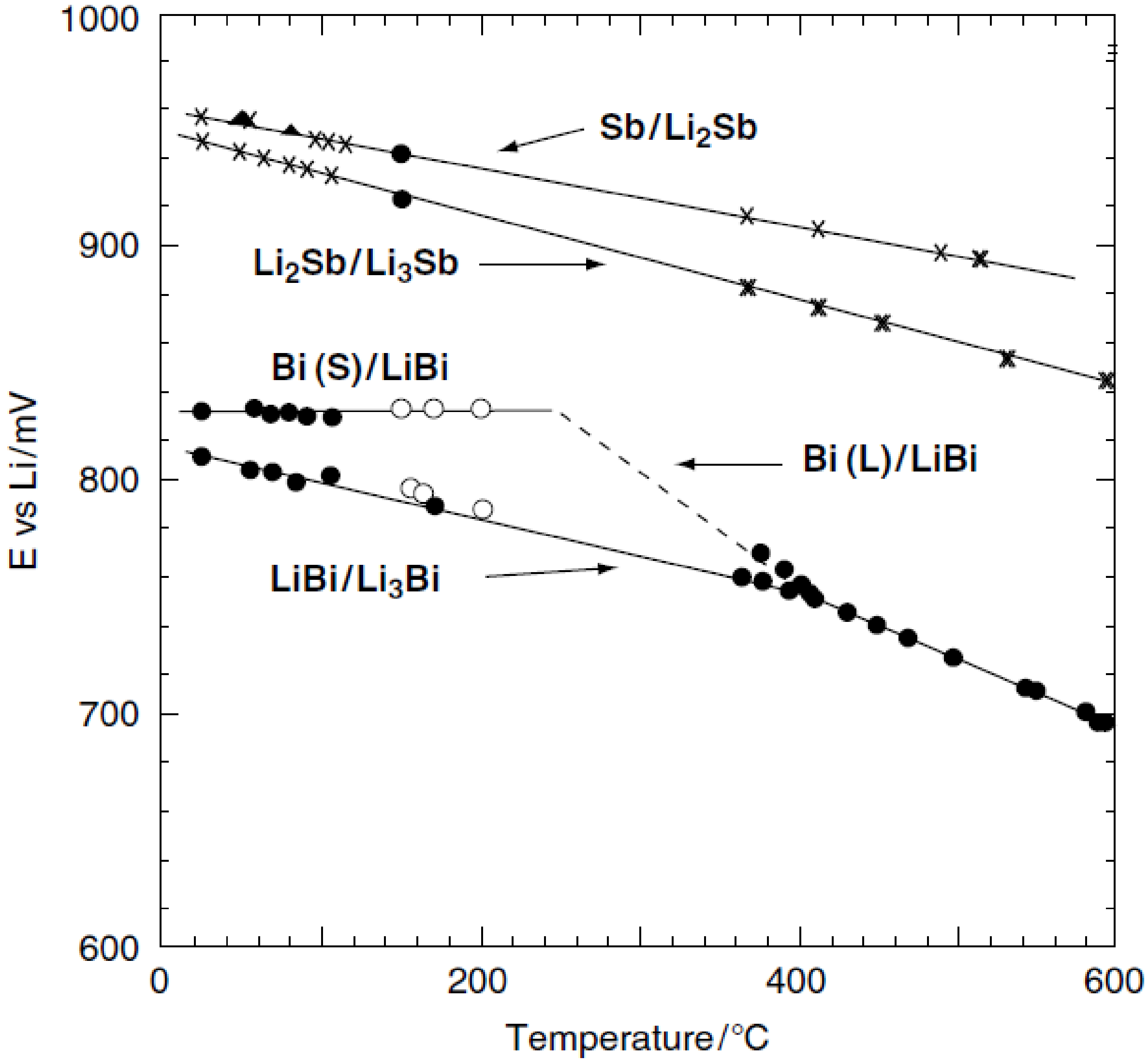

Fig. 3.16 Temperature dependence of the potentials of the two-phase plateaus in the Li–Sb and Li–Bi systems, [12]

Table 3.1 Reaction entropies in the lithium–antimony and lithium–bismuth systems

Reaction	Molar entropy of reaction (J/K mol)	Temperature range (°C)
$2Li + Sb = Li_2Sb$	−31.9	25–500
$Li + Li_2Sb = Li_3Sb$	−46.5	25–600
$Li + Bi = LiBi$	0	25–200
$2Li + LiBi = Li_3Bi$	−36.4	25–400

-the temperature dependence of the value of ΔG_r°, is evident from the relation between the Gibbs free energy, the enthalpy, and the entropy

$$\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$$

where ΔH_r° is the change in the standard enthalpy and ΔS_r° is the change in the standard entropy resulting from the reaction. Thus it can be seen that

$$d\Delta G_r^\circ/dT = \Delta S_r^\circ$$

From such data, the value of the standard molar entropy changes involved in these several reactions is obtained.

5. Application to oxides and similar materials – metal-oxygen system

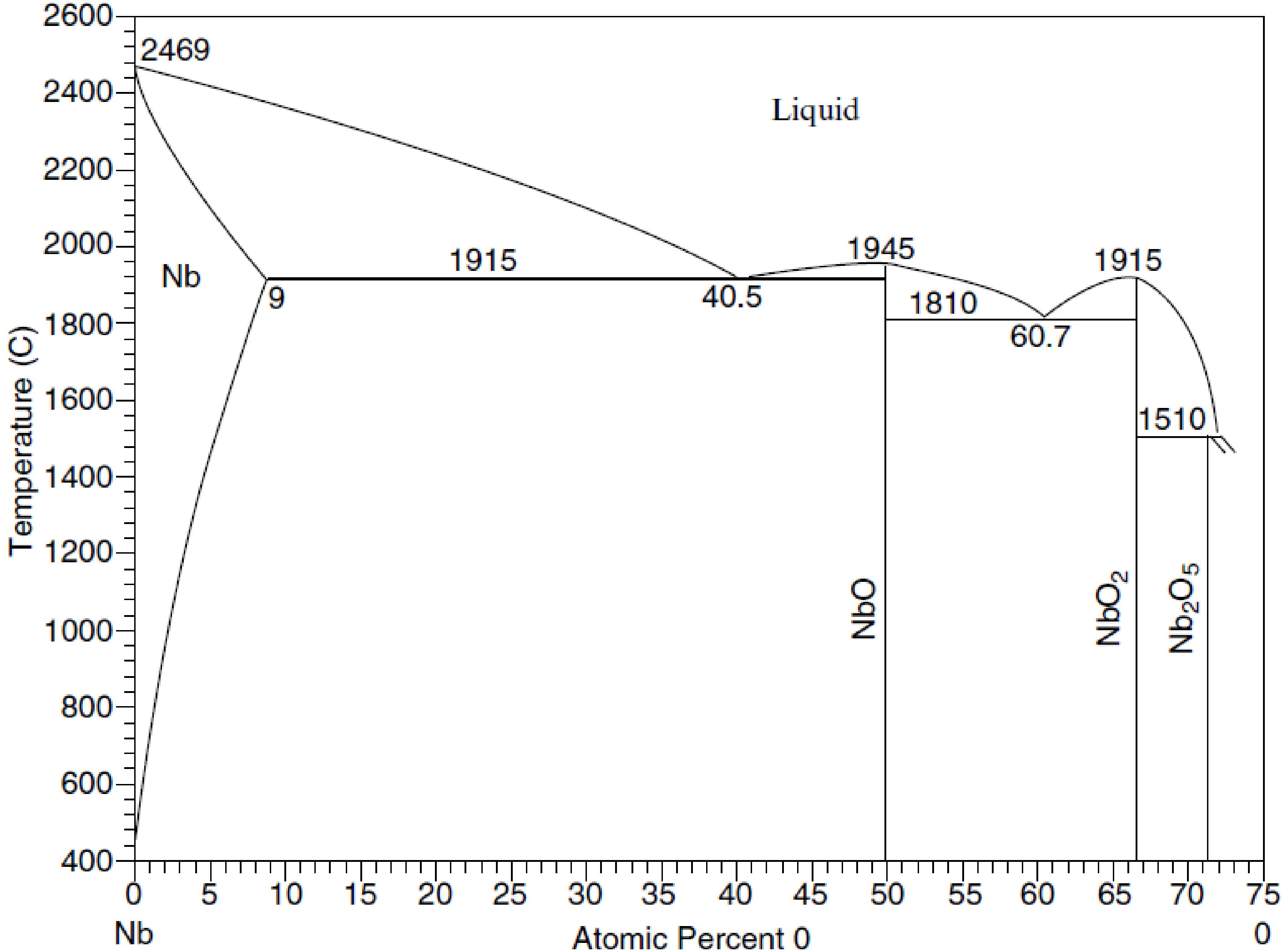

Fig. 3.17 Niobium–oxygen phase diagram

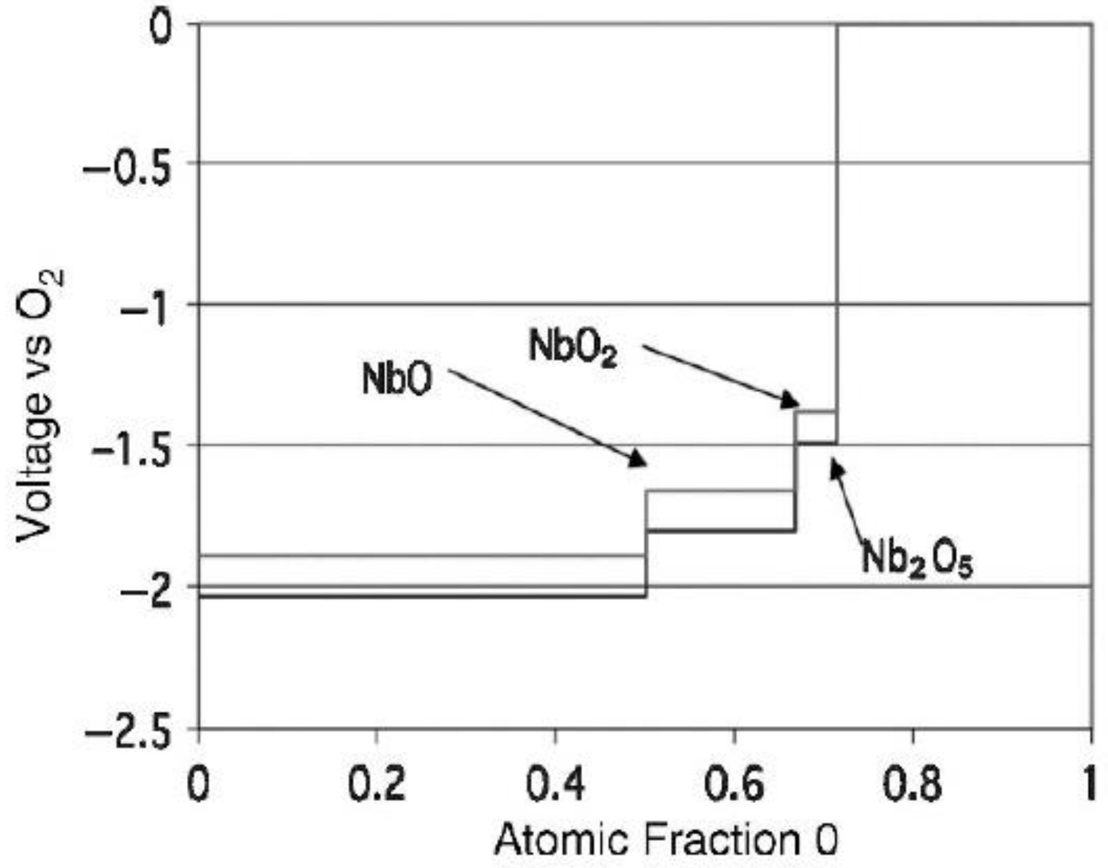

Fig. 3.18 Equilibrium potentials of the three two-phase plateaus in the Nb–O system at two temperatures

6. Ellingham diagrams (엘링감 도표)

plots of the Gibbs free energy
of formation of their oxides as a function of temperature

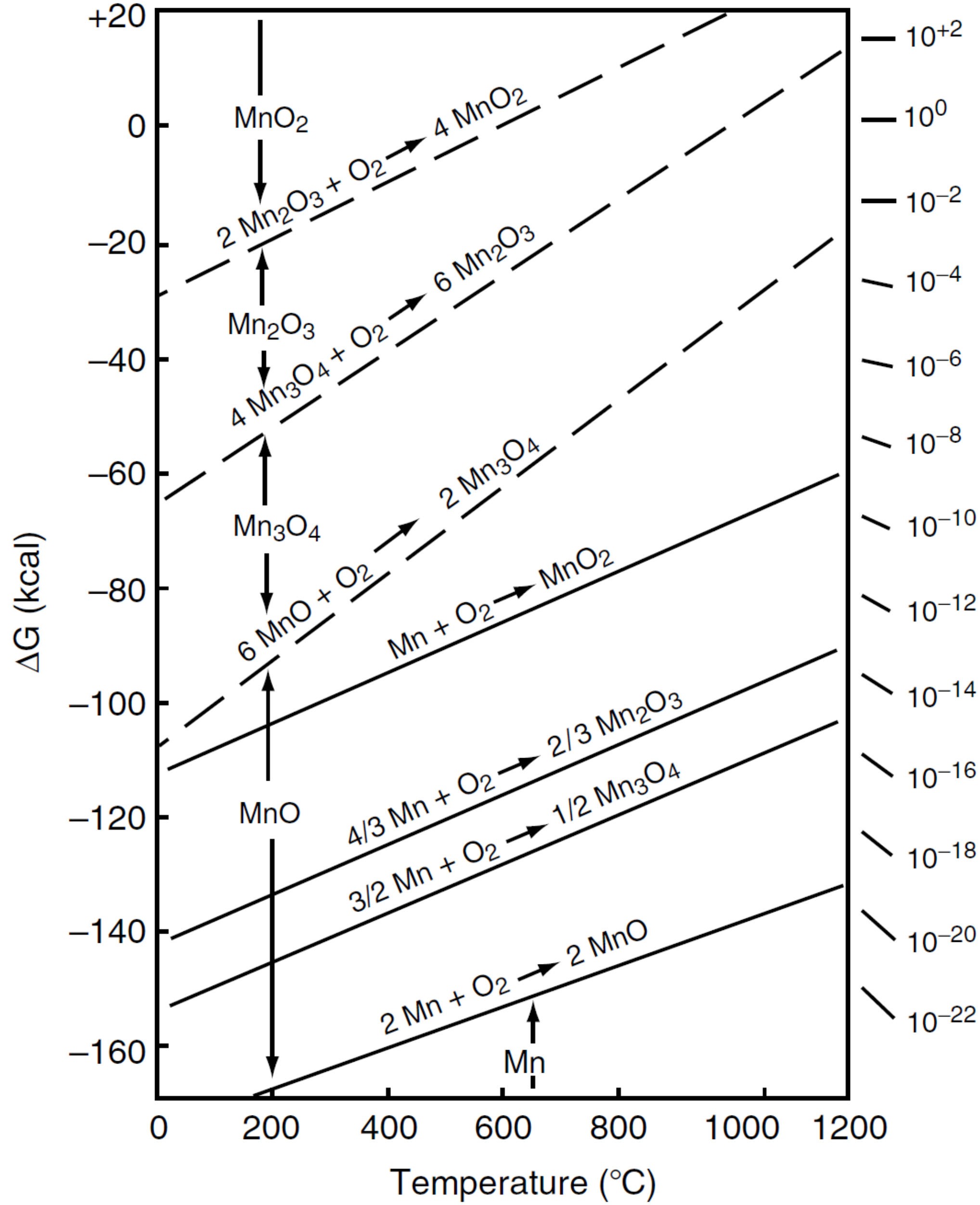

Fig. 3.19 Ellingham type diagram that shows both integral and difference data for the manganese oxide system [14]

7. Liquid binary electrode

Na-S battery at 300℃

Both electrodes are liquid (molten sodium, liquid sulfur)

Electrolyte : sodium beta alumina (solid Li electrolyte)

L/S/L system

$xNa + S = Na_xS$

Two phase → single phase

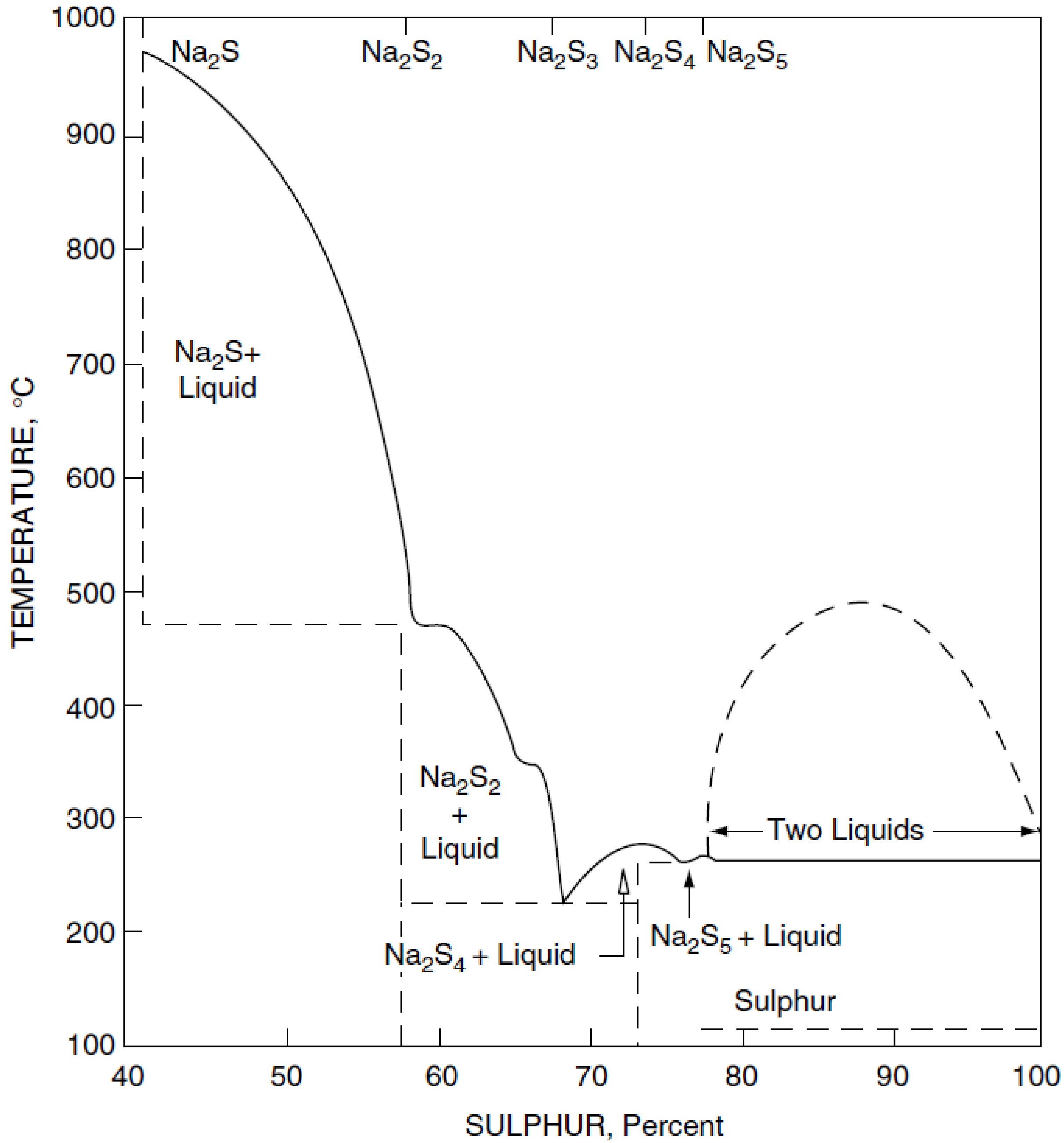

Fig. 3.20 Part of the sodium–sulfur phase diagram

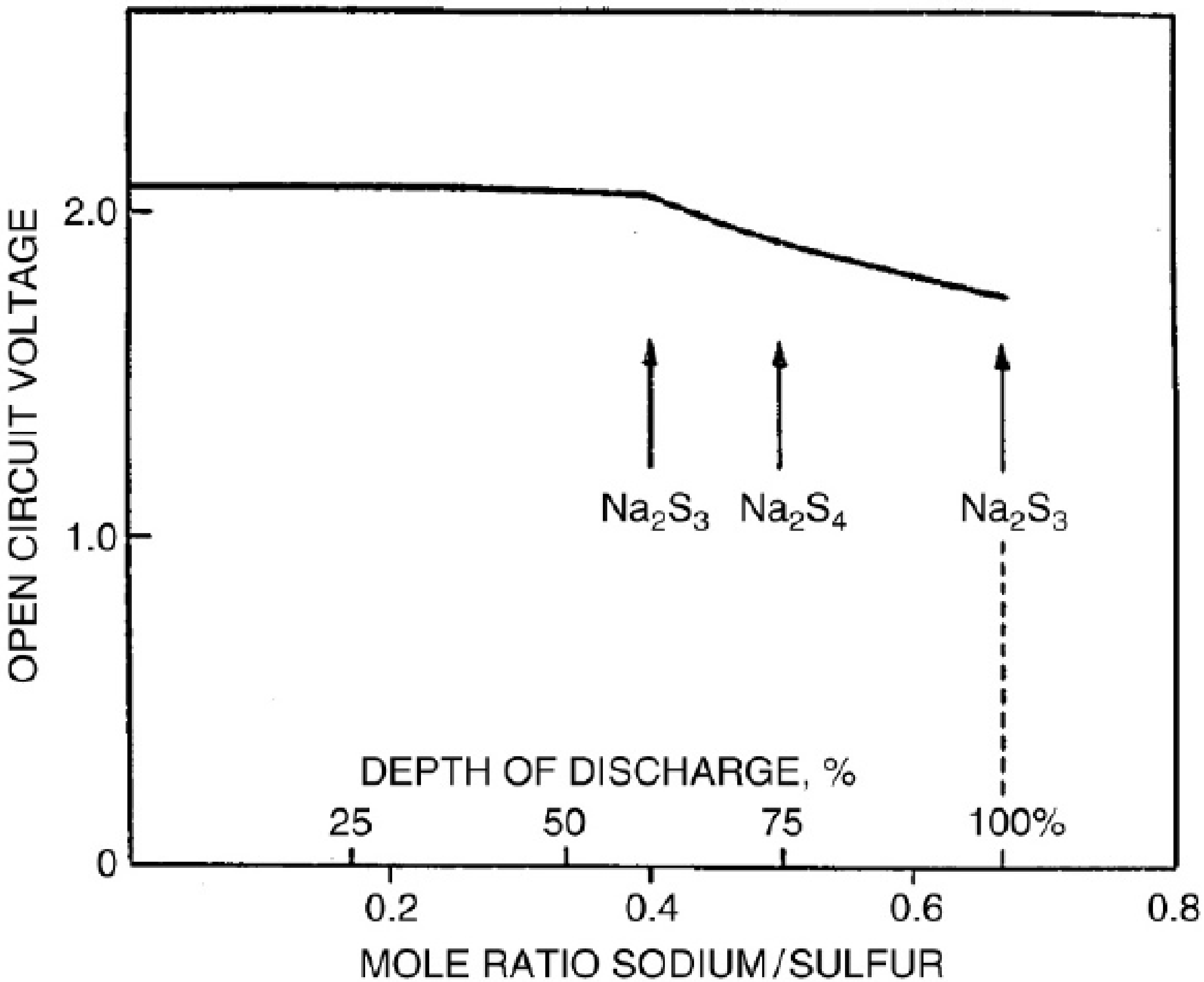

Fig. 3.21 Voltage versus pure sodium as a function of composition