

Theoretical Analysis of Binary (Solid/Liquid) Phase Diagrams for Two Metals

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Abstract

Thermal equilibrium diagrams (phase diagrams) give informations on the phases present and their compositions at equilibrium in alloy systems. A knowledge of thermodynamic stability of molecular structure has an important effect for understanding phase transformations in materials which are represented in phase diagrams. Theoretical method of calculating phase diagrams by using thermodynamic properties is using in this work. Phase diagrams of two metals completely soluble in liquid and solid state with assuming that diagrams without miscibility gap are considered as diagrams of ideal solution while with miscibility gap are considered as diagrams of regular solutions. By comparing the results obtained from the theoretical method by computer program with the experimental method by using the thermal analysis which are considered as standard diagrams in all references. The maximum difference between theoretical and experimental diagrams is 40%. The minimum difference between them is 0.086%.

الخلاصة

مخططات التوازن الحراري (مخططات الأطوار) تعطي معلومات عن الأطوار الموجودة و تراكيبها عند الاتزان في أنظمة السبائك. إن لمعرفة الاستقرارية الترموديناميكية للتركيب الجزيئي تأثير مهم في فهم التحولات الطورية للمعادن و السبائك التي تتضح في مخططات الأطوار. حسب مخططات الأطوار في هذا البحث بالاعتماد على الطريقة النظرية باستخدام الخواص الترموديناميكية. مخططات الأطوار لمعدنين لهما القابلية على الذوبانية بشكل تام في الحالتين السائلة و الصلبة مع افتراض أن المخططات الحاوية على فجوة امتزاجية تعامل كمخططات للمحاليل المنتظمة و التي لا تمتلك فجوة امتزاجية تعتبر كمخططات للمحاليل المثالية. بمقارنة النتائج التي تم الحصول عليها من الطريقة النظرية بواسطة تصميم برنامج مع المخططات التجريبية باستخدام التحليل الحراري والتي تعتبر مخططات قياسية ثابتة في جميع المصادر، وجد أن أكبر نسبة اختلاف بين المخططات النظرية و العملية هي 40% وأقل نسبة اختلاف هي 0.086%.

1-Introduction:

The phase diagram is a convenient graphical method of displaying the state of a given system that is stable under a defined set of conditions[Grant,1980]. The main idea of phase diagrams is based around the latent heat that is evolved when a mixture is cooled, and the phase is changed[Zaineab,2005]. The equilibrium state is the state of minimum free energy of the binary system at a given temperature and composition at constant pressure[Kittle,1996]. Phase diagrams enable to predict what phases are in equilibrium for selected alloy compositions at desired temperatures, determine the chemical composition of each phase, and calculate the quantity of each phase present[Vanvlack,1982].

A system consists of two metals have the same crystal structure, and they are chemically and physically very much alike, is called isomorphous system[Zaineab,2005]. In one component system melting occurs at a well defined melting temperature. In multi-component systems melting occurs over a range of temperatures between the solidus and liquidus lines. Solid and liquid phases are in equilibrium in this temperature range [Zhigilei,2002]. Copper- nickel and germanium-silicon are phase diagrams of this type.

For phase diagrams of real solution there is the difference between the actual free energy of the solution and the value the free energy would have if the solution were ideal[Zaineab,2005], thus at low temperatures, there is a region where the solid solution is most stable as a mixture of two phases because of slow diffusion and difficulty in attaining equilibrium, this region is called a miscibility gap[Zhigilei,2002].

2-Theoretical Analysis:

Theoretical calculation of phase diagrams by using thermodynamic properties is more important than experimental method as:-

- 1-Calculations involving solid phases are more manageable than, for instance, those involving liquid phases.
- 2-The determination of the solid state part of a phase diagram in experimental method is most likely to be hindered by sluggish kinetics or characterization problems.
- 3-It enables to predict some features of the system which are not easily measured, as well as to predict phase diagrams of complex multi-component systems. The time is reduced by using the theoretical method.
- 4-Calculations involving solid phases are more manageable than, for instance, those involving liquid phases.
- 5-The determination of the solid state part of a phase diagram in experimental method is most likely to be hindered by sluggish kinetics or characterization problems.
- 6-It enables to predict some features of the system which are not easily measured, as well as to predict phase diagrams of complex multi-component systems.
- 7-It will be easy to draw the phase diagrams of refractory metals.[Gleb,2002]

3-Theoretical Calculation of Binary Phase Diagram :-

To conclude phase diagrams of two metals completely soluble in liquid and solid state by using Gibbs free energy of the liquid and the solid states to find the equilibrium between two phases [Zaïneb,2005].For equilibrium in a system the chemical potential of any component in all phases[Zhigilei,2002].

$$G^L = X_A^L G_A^L + X_B^L G_B^L + \Delta G^{XS} + RT(X_A^L \ln X_A^L + X_B^L \ln X_B^L) \quad (1)$$

where:

$$\Delta G^{XS} = \Delta H^{XS} + \Delta S^{XS} \quad (2)$$

3.1Phase diagrams for ideal solution

Real systems which behave almost ideally in both the solid and liquid states present the possibility of the relatively simple quantitative calculation of phase diagrams. The excess Gibbs free energy is zero for ideal solution. The equations for the liquidus and solidus curves in the systems of two metals soluble completely in liquid and solid states will be developed from the relations in [Zaïneb,2005]:-

$$G^L = G^{M,L} + RT(X_A^L \ln X_A^L + X_B^L \ln X_B^L) \quad (4)$$

G^{M,L}
in
turn

may be written as:

$$G^{M,L} = (X_A^L G_A^L + X_B^L G_B^L) \quad (5)$$

The
free

energy of the liquid solution as a function of partial molal free energy is:-

$$G^L = (\mu_A^L X_A^L + \mu_B^L X_B^L) \quad (6)$$

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$$dG^L = (\mu_A^L dX_A^L + \mu_B^L dX_B^L) \quad (7)$$

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B in the solution at equilibrium is concluded from the next equations ,by substituting $X_A=1-X_B$ and $dX_A=-dX_B$, combining equations (6)and (7), and suitably rearranging as:

$$\mu_B^L = G^L + X_A^L \frac{dG^L}{dX_B^L} \quad (8) \quad \text{At a}$$

$$\mu_A^L = G^L - X_B^L \frac{dG^L}{dX_B^L} \quad (9) \quad \Delta G_B = \Delta H_B - T\Delta S_B \quad (13)$$

Thus the chemical potential of metal B in the liquid phase is:

$$\mu_B^L = G_B^L + RT \ln X_B^L \quad (10)$$

In an analogous manner in the solid solution:

$$\mu_B^S = G_B^S + RT \ln X_B^S \quad (11)$$

If the liquid and solid solutions are to be in equilibrium, the chemical potentials of B in each must be identical; equating (10) and (11):-

$$RT \ln \frac{X_B^S}{X_B^L} = G_B^L - G_B^S = \Delta G_B \quad (12)$$

given temperature the difference in Gibbs free energy for metal B is:

When B melts under equilibrium conditions at constant temperature and pressure. At melting temperature the change in Gibbs free energy is zero:

Assuming that neither ΔS_B nor ΔH_B varies with temperature, this is equivalent to assuming

$$\Delta G_B^m = 0 = \Delta H_B^m - T_B^m \Delta S_B^m \quad \text{or} \quad \Delta S_B^m = \frac{\Delta H_B^m}{T_B^m} \quad (14)$$

that the difference between the heat capacity of the liquid and that of the solid, ΔC_p , does not change with temperature [Saunders, 1996]:

$$\Delta S_B = \Delta S_B^m \quad \text{and} \quad \Delta H_B = \Delta H_B^m \quad (15) \quad \begin{array}{l} \text{then} \\ \text{substituted} \end{array}$$

ion of Eq.(15) into (14) gives:-

$$\Delta G_B = \Delta H_B^m - T \frac{\Delta H_B^m}{T_B^m} = \Delta H_B^m \left(1 - \frac{T}{T_B^m}\right) \quad (16)$$

By combining Eqs.(12) and (16) it can be found:

$$\ln \frac{X_B^S}{X_B^L} = \frac{\Delta H_B^m}{R} \left(\frac{1}{T} - \frac{1}{T_B^m} \right) \quad (17)$$

The same, analysis obviously holds for the component A in the two solutions so that:

$$\ln \frac{1 - X_B^S}{1 - X_B^L} = \frac{\Delta H_A^m}{R} \left(\frac{1}{T} - \frac{1}{T_A^m} \right) \quad (18)$$

In this work , by assuming that metals melt and solidify at their melting temperature under equilibrium conditions, that is $\Delta G=0$, and using Eqs. (17) and (18) to calculate the solidus and liquidus curves for ideal solutions (isomorphous systems). The equilibrium melting temperature and the enthalpy of fusion at constant pressure of the pure components at their melting points are needed to determine this type of phase diagrams.

3.2 Solidus and Liquidus Curves for Regular Solution:-

Depending on chemical potentials of components at equilibrium of phase diagram, two equations to determine the solidus and liquidus curves of regular solutions concerning on X_B^S and X_B^L . It is assumed that the enthalpy of each component at any temperature is equal to its enthalpy of fusion at its melting temperature; and that is true for the entropy. The regular solution has the excess Gibbs free energy which represent excess enthalpy and excess entropy. The excess entropy is negligibly small. Thus it equals zero. At equilibrium:

$$\mu_B^L = \mu_B^S \quad \text{and} \quad \mu_A^L = \mu_A^S \quad \text{Thus for determining the mole fractions of metal B}$$

For regular solution: $\Delta S_{xs}=0$; $\Delta G_{xs}=\Delta H_{xs}$

The excess enthalpy as a function to critical temperature .The critical temperature is the beginning of miscibility gap:-

$$\Delta H^{xs}=2RT_c X_A X_B \quad (19)$$

in the liquid and in the solid solution by the next method. Gibbs free energy of liquid solution in regular system is:

$$G^L = X_A^L G_A^L + X_B^L G_B^L + 2RT_c X_A^L X_B^L + RT(X_A^L \ln X_A^L + X_B^L \ln X_B^L) \quad (20)$$

The differentiation of Eq.(20) is:-

$$\frac{dG^L}{dX_B^L} = G_B^L - G_A^L + 2RT_c - 4RT_c X_B^L + RT \ln \frac{X_B^L}{X_A^L} \quad (21)$$

For metal A:

$$\mu_A^L = G^L - X_B^L \frac{dG^L}{dX_B^L} = G_A^L + 2RT_c (X_B^L)^2 + RT \ln(X_A^L) \quad (22)$$

For solid solution:

$$G^S = X_A^S G_A^S + X_B^S G_B^S + 2RT_c X_A^S X_B^S + RT(X_A^S \ln X_A^S + X_B^S \ln X_B^S) \quad (23)$$

$$\frac{dG^S}{dX_B^S} = G_B^S - G_A^S + 2RT_c - 4RT_c X_B^S + RT \ln \frac{X_B^S}{X_B^L} \quad (24)$$

From Eqs.(23)and(24)the chemical potential of metal A is in solid solution is:

At equilibrium $\mu_A^L = \mu_A^S$, then $\mu_A^L - \mu_A^S = 0$, from Eqs.(22)and(25) For

metal B, by the same way:

$$RT \ln \frac{X_B^S}{X_B^L} = \Delta G_B^S + 2RT_c \left((X_B^L)^2 (X_A^S)^2 + 2(X_B^S - X_B^L) \right) \quad (26)$$

The miscibility

gap can be calculated by knowing its critical temperature and using Eq.(28) :-

$$T = \frac{2(1 - 2X_B^S)T_c}{\ln[(1 - X_B^S)/X_B^S]} \quad (28)$$

Thus the enthalpy of fusion of each component and its melting temperature, and the critical temperature which represent the beginning of the miscibility gap of the system are required. Primary values of X_B^S and X_B^L must be known and these variables are independent.

4 Application (Results and Discussion):-

1-For phase diagrams of first type:-

Copper-Nickel[Cu-Ni]:Theoretical solidus line is less than that of experimental solidus line [Vacro,1996]in the region between (0-0.16)mole fraction of Ni with maximum difference of $10^\circ K$ at $X_{Ni}=0.08$,when $T_{exp.}=1385^\circ K$ and $T_{th.}=1375^\circ K$,while it will be higher in the region between(0.22-0.61)with maximum difference of $10^\circ K$ at $X_{Ni}=0.5$,when $T_{exp.}=1530^\circ K$ and $T_{th.}=1540^\circ K$.Except these regions two lines are identical. Experimentally liquidus line[Vacro,1996] for all alloys is higher than theoretical liquidus line with maximum difference of $50^\circ K$ at $X_{Ni}=0.4$,when $T_{exp.}=1545^\circ K$, and $T_{th.}=1495^\circ K$.

Germanium-Silicon[Ge-Si]:Ending melting temperatures in theoretical method lower than that in experimental method [Allan,1996]with maximum difference in temperature is $50^\circ K$ at $wt_{Si}=0.27$,when $T_{exp.}=1540^\circ K$ and $T_{th.}=1490^\circ K$.Theoretical and experimental solidus lines are identical in the region between(0.1-0.67)but in other regions theoretical solidus line higher than that in experimental [Allan,1996]with maximum difference in temperature is $15^\circ K$ at $wt_{Si}=0.93$,when $T_{exp.}=1675^\circ K$ and $T_{th.}=1680^\circ K$.

Ruthenium-Osmium[Ru-Os]:Theoretical solidus and liquidus lines are identical to that of experimental [Rapperort,2000]in the region (0-0.12)for the first and (0-0.09) for the second. For theoretical method all alloys with mole fraction greater than 0.42 start melting at temperatures higher than that for experimental method [Rapperort,2000]with maximum difference of $20^\circ K$ at $X_{Os}=0.46$,when $T_{exp.}=2870^\circ K$ and $T_{th.}=2890^\circ K$.The ending melting temperature for alloys by theoretical method are lower than that of alloys by experimental method [Rapperort,2000]with maximum difference of $20^\circ K$ at $X_{Os}=0.17$,when $T_{exp.}=2710^\circ K$ and $T_{th.}=2680^\circ K$.Theoretical and experimental [Rapperort,2000]liquidus lines

are identical in the region between (0.28-0.32), but alloys in theoretical method complete their melting at temperatures higher than that of alloys in experimental method [Rapperort, 2000] with maximum difference of 20°K at $X_{\text{Os}}=0.4$, when $T_{\text{exp.}}=2860^{\circ}\text{K}$ and $T_{\text{th.}}=2880^{\circ}\text{K}$, then the two lines are identical from (0.9-1).

Silver-Palladium[Ag-Pd]: Experimental solidus line [web, 1996] and theoretical liquidus line are identical in two regions (0-0.06) and (0.47-1). The maximum difference between theoretical liquidus line and experimental liquidus line is 75°K at $X_{\text{Pd}}=0.8$, when $T_{\text{exp.}}=1780^{\circ}\text{K}$, and $T_{\text{th.}}=1705^{\circ}\text{K}$ but for solidus line is 80°K at $X_{\text{Pd}}=0.2$, when $T_{\text{exp.}}=1400^{\circ}\text{K}$ and $T_{\text{th.}}=1320^{\circ}\text{K}$.

Approximately theoretical and experimental solidus lines in some regions are identical for Cu-Ni, Ge-Si, and Ru-Os but differ in other regions with percentage 2%, 0.086%, and 1% respectively. For Ag-Pd starting melting temperatures in theoretical method less than that in experimental method with maximum percentage is 9%. Ending melting temperatures in experimental method higher than that in theoretical method for Cu-Ni, Ge-Si, and Ag-Pd with percentage 4%, 6%, and 7% respectively, but for Ru-Os in some regions these temperatures identical but for other theoretical ending temperatures higher than that in experimental with percentage 2%.

The increasing or decreasing values because the assumptions that solution is ideal when the molecules of two metals have similar size and attract one another with the same force, all metals melt and solidify at their melting temperatures under equilibrium conditions that is the difference in Gibbs free energy is zero at the melting temperature, and the difference between the heat capacity of the liquid and that of the solid, ΔC_{pr} does not vary with temperature.

2-For all phase diagrams of second type:-

Gold-Platinum[Au-Pt]: Solidus lines by theoretical and experimental [Rapperort, 2000] manners are identical in the region (0-0.74), while there is 110°K difference at $X_{\text{Pt}}=0.9$, when $T_{\text{exp.}}=1880^{\circ}\text{K}$ and $T_{\text{th.}}=1990^{\circ}\text{K}$. Liquidus lines are identical in the region (0-0.1) while the maximum difference reaches 90°K at $X_{\text{Pt}}=0.28$, when $T_{\text{exp.}}=1700^{\circ}\text{K}$ and $T_{\text{th.}}=1790^{\circ}\text{K}$. Maximum temperature for the theoretical miscibility gap is $T_{\text{th.}}=1529.8^{\circ}\text{K}$ at $X_{\text{Pt}}=0.51$ but that for experimental [Rapperort, 2000] is $T_{\text{exp.}}=1523^{\circ}\text{K}$ at $X_{\text{Pt}}=0.6$.

Iridium-Palladium[Ir-Pd]: Alloys in experimental method [Tripathi, 1991] start to fuse at temperature less than that analyzed by theoretical method with maximum difference between them is 750°K at $X_{\text{Ir}}=0.6$, when $T_{\text{exp.}}=2000^{\circ}\text{K}$ and $T_{\text{th.}}=2750^{\circ}\text{K}$. Ending melting temperature for alloys by theoretical method are higher than that alloys by experimental method [Tripathi, 1991] with maximum difference of 400°K at $X_{\text{Ir}}=0.34$, when $T_{\text{exp.}}=1960^{\circ}\text{K}$ and $T_{\text{th.}}=2300^{\circ}\text{K}$. Top of theoretical and experimental [Tripathi, 1991] miscibility gap being at $X_{\text{Ir}}=0.5$ but there is 300°K difference when $T_{\text{th.}}=1500^{\circ}\text{K}$ and $T_{\text{exp.}}=1800^{\circ}\text{K}$.

Niobium-Tungsten[Nb-W]: By comparing results of theoretical and experimental method, it is noted that the theoretical and experimental [Poulsen, 2003] solidus lines are identical in the region (0-0.14) but wherever X_{W} is more than 0.41 starting of melting of alloys by theoretical method is lower than that of alloys by experimental method [Poulsen, 2003] with maximum difference of 60°K at $X_{\text{W}}=0.81$, when $T_{\text{exp.}}=3300^{\circ}\text{K}$ and $T_{\text{th.}}=3240^{\circ}\text{K}$. Maximum difference for ending temperature in the two methods is 430°K at $X_{\text{W}}=0.4$, when $T_{\text{exp.}}=3000^{\circ}\text{K}$ and $T_{\text{th.}}=3430^{\circ}\text{K}$. There are two points of intersection: $X_{\text{W}}=0.22$, $T=353.5^{\circ}\text{K}$ and $X_{\text{W}}=0.77$, $T=356^{\circ}\text{K}$. The highest temperature for experimental method [Poulsen, 2003] is 550°K at $X_{\text{W}}=0.5$, while for is 398°K at $X_{\text{W}}=0.57$.

Palladium-Rhodium[Pd-Rh]: Starting temperature and ending temperature of fusion for alloys by experimental method is lower than that for alloys by theoretical method with maximum difference of 70°K at $X_{\text{Rh}}=0.28$, when $T_{\text{exp.}}=1850^{\circ}\text{K}$ and $T_{\text{th.}}=1920^{\circ}\text{K}$ for starting and 40°K at $X_{\text{Rh}}=0.3$, when $T_{\text{exp.}}=1990^{\circ}\text{K}$ and $T_{\text{th.}}=1950^{\circ}\text{K}$ for ending. Experimental miscibility gap [Poulsen, 2003] is higher than theoretical miscibility gap with maximum difference of 290°K at $X_{\text{Rh}}=0.5$ when $T_{\text{exp.}}=1190^{\circ}\text{K}$ and $T_{\text{th.}}=900^{\circ}\text{K}$.

Approximately theoretical liquidus line higher than that in experimental method with maximum percentage is 26% for Nb-W. Theoretical and experimental solidus lines for Au-Pt and Nb-W are identical until $X_{\text{Au}}=0.77$ and $X_{\text{W}}=0.4$ after that differ with percentage of 6% and 2% respectively, but for Pd-Ir and Pd-Rh experimental solidus line lower than that in theoretical method with percentage of 2% and 9.4% respectively. For all diagrams experimental miscibility gap is higher than theoretical miscibility gap but for Au-Pt experimental and theoretical miscibility gaps intersect at $X_{\text{Au}}=0.6$. These differences between theoretical and experimental methods because: using excess enthalpy which represent deviation from ideality as a function of critical temperature, assuming interaction energy between atoms of metal A is equal to the interaction energy between atoms of metal B, interaction energy between pair of atoms as a function to the critical temperature of miscibility gap, using critical temperature for miscibility gap from experimental diagram, and initial values of mole fractions as input in computer program.

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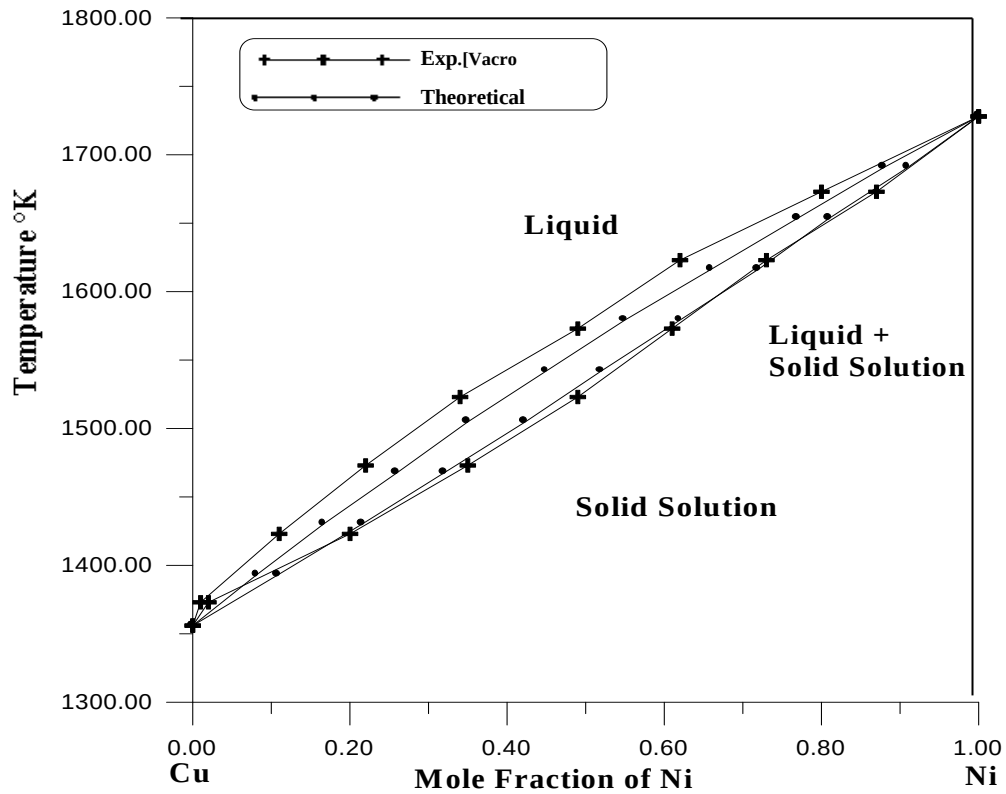


Fig.(1):Phase diagram of copper –nickel.

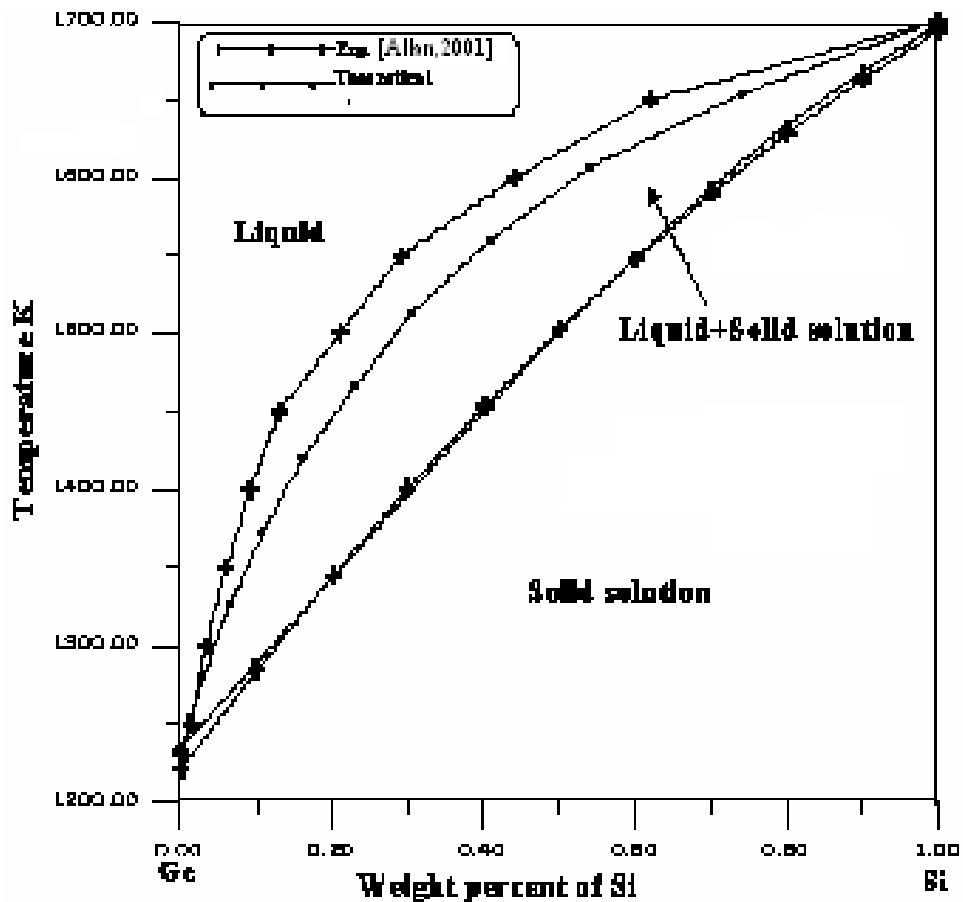


Fig.(2):Phase diagram of germanium- silicon

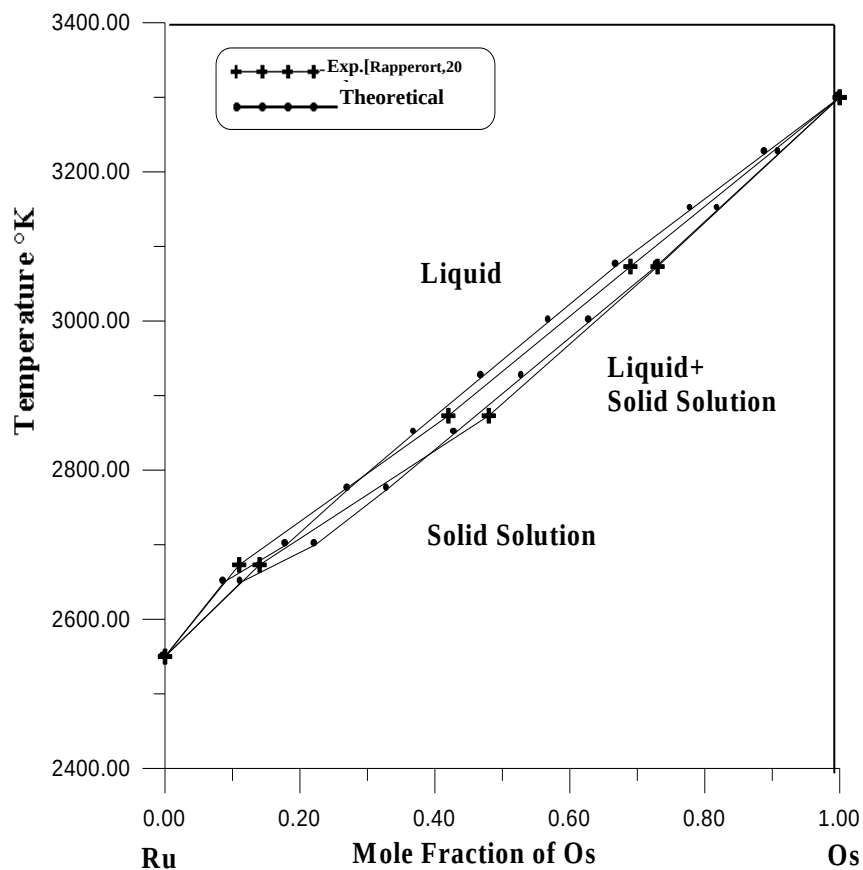


Fig.(3):Phase diagram of ruthenium-

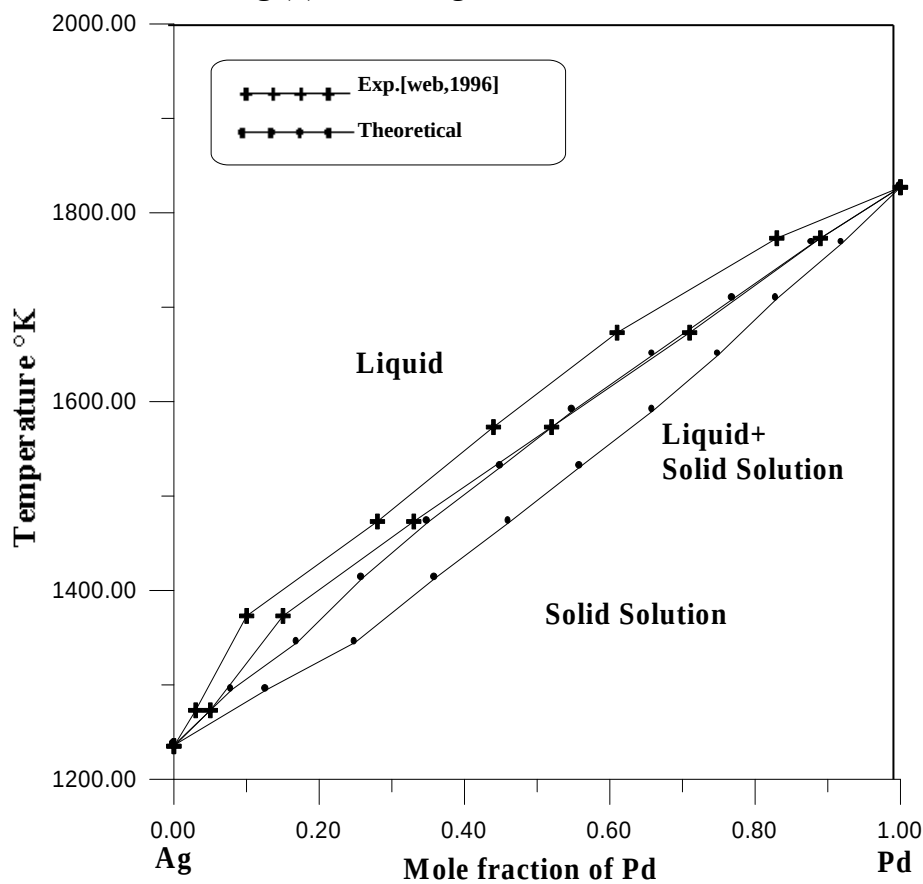


Fig.(4):Phase diagram of silver-palladium.

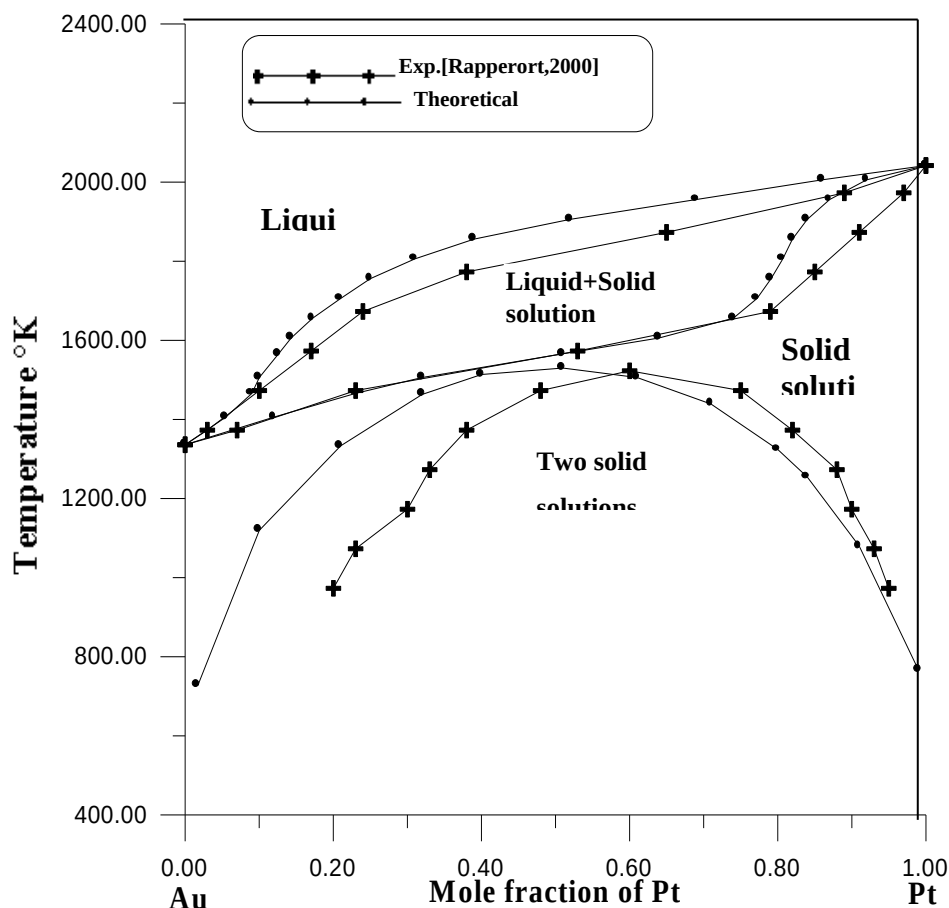


Fig.(5):Phase diagram of gold-platinum.

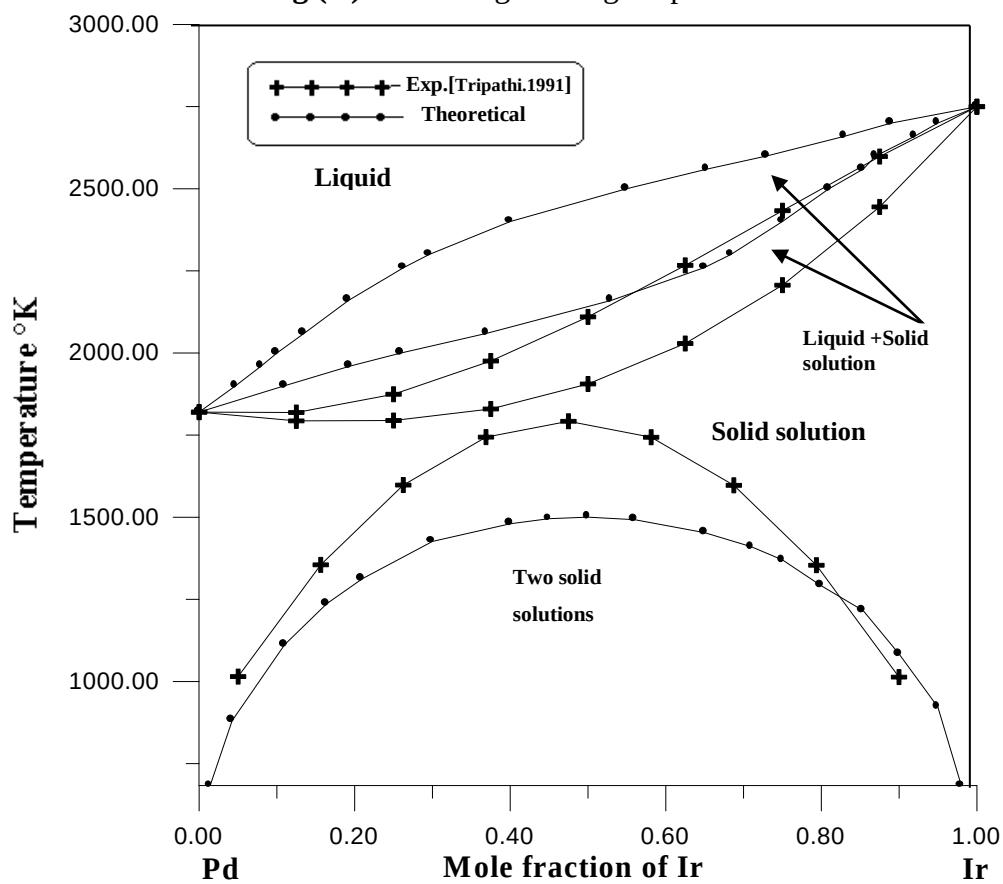


Fig.(6):Phase diagram of iridium-palladium.

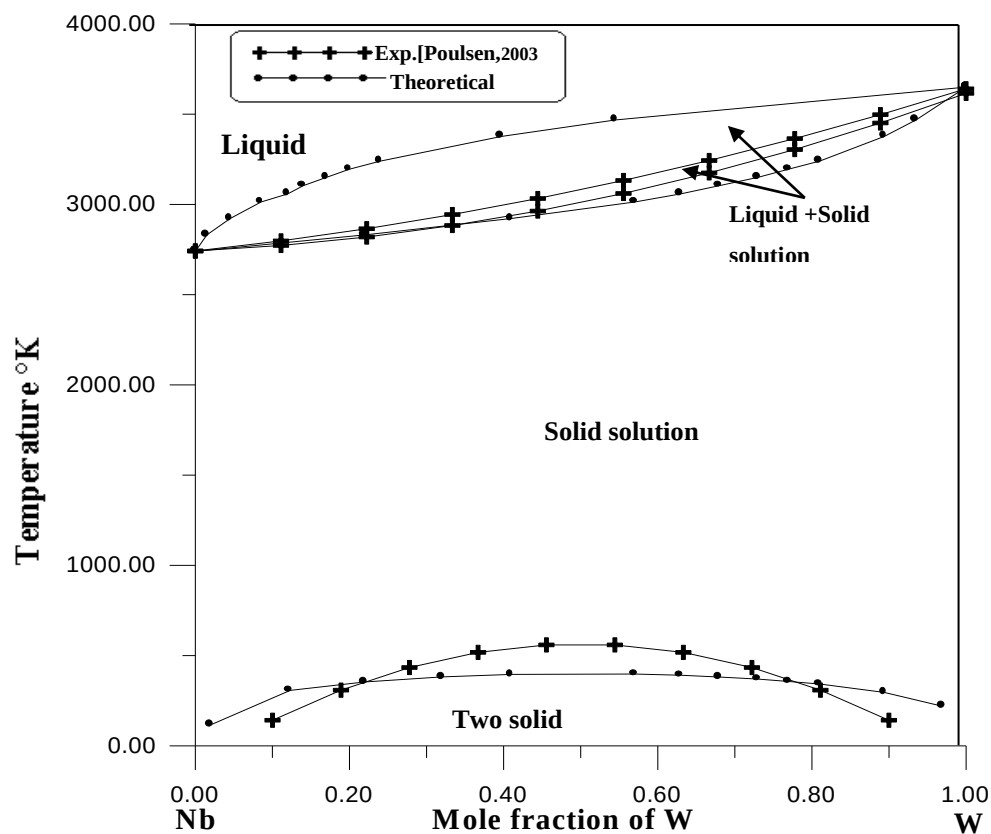


Fig.(7):Phase diagram of niobium-tungsten.

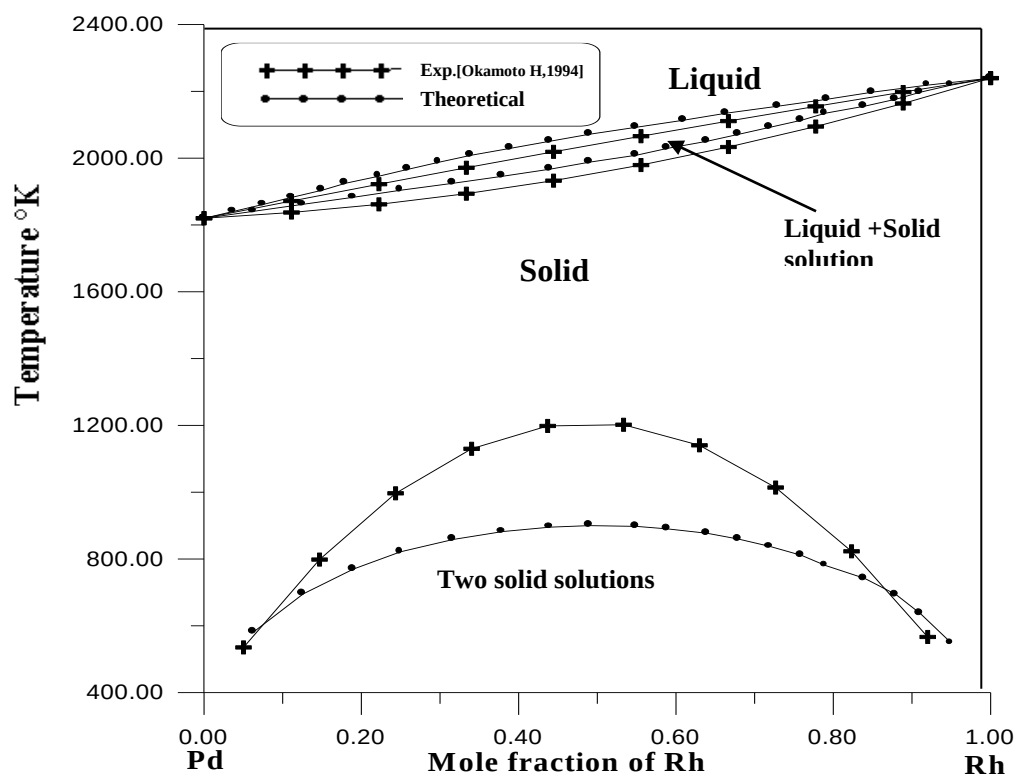


Fig.(8):Phase diagram of palladium- rhodium.