Gibbs Energies of Formation of Intermetallic Phases in the Systems Pt-Mg, Pt-Ca, and Pt-Ba and Some Applications

K.T. JACOB, K.P. ABRAHAM, and S. RAMACHANDRAN

The standard Gibbs energies of formation of platinum-rich intermetallic compounds in the systems Pt-Mg, Pt-Ca, and Pt-Ba have been measured in the temperature range of 950 to 1200 K using solid-state galvanic cells based on MgF_2, CaF_2, and BaF_2 as solid electrolytes. The results are summarized by the following equations:

$$\Delta G^\circ\,(MgPt_7) = -256{,}100 + 16.5T\,(\pm 2000)\quad J/mol$$

$$\Delta G^\circ\,(MgPt_3) = -217{,}400 + 10.7T\,(\pm 2000)\quad J/mol$$

$$\Delta G^\circ\,(CaPt_5) = -297{,}500 + 13.0T\,(\pm 5000)\quad J/mol$$

$$\Delta G^\circ\,(Ca_2Pt_7) = -551{,}800 + 22.3T\,(\pm 5000)\quad J/mol$$

$$\Delta G^\circ\,(CaPt_2) = -245{,}400 + 9.3T\,(\pm 5000)\quad J/mol$$

$$\Delta G^\circ\,(BaPt_5) = -238{,}700 + 8.1T\,(\pm 4000)\quad J/mol$$

$$\Delta G^\circ\,(BaPt_2) = -197{,}300 + 4.0T\,(\pm 4000)\quad J/mol$$

where solid platinum and liquid alkaline earth metals are selected as the standard states. The relatively large error estimates reflect the uncertainties in the auxiliary thermodynamic data used in the calculation. Because of the strong interaction between platinum and alkaline earth metals, it is possible to reduce oxides of Group IIA metals by hydrogen at high temperature in the presence of platinum. The alkaline earth metals can be recovered from the resulting intermetallic compounds by distillation, regenerating platinum for recycling. The platinum-slag-gas equilibration technique for the study of the activities of FeO, MnO, or Cr_2O_3 in slags containing MgO, CaO, or BaO is feasible provided oxygen partial pressure in the gas is maintained above that corresponding to the coexistence of Fe and "FeO."

I. INTRODUCTION

SINCE the early studies of Abraham *et al.*[1] on the activity of MnO in MnO-SiO_2 slags, the platinum-slag-gas equilibrium technique has been extensively used for the measurement of activities of FeO, MnO, and Cr_2O_3 in slags.[2,3,4] At an oxygen potential fixed by the gas phase, the less stable compound, such as MnO, in the slag is partially reduced and forms a solid solution with platinum. If the equilibrium concentration of manganese in platinum is measured, the activity of MnO in the slag can be derived using the standard Gibbs energy of formation of MnO and the known activity-composition relationship in the Pt-Mn system. Because of the absence of activity data in ternary or higher order solid solutions such as Pt-Mn-Fe, the technique has been traditionally limited to slags in which only one component can be easily reduced into platinum. Even some of the more stable components in slags such as MgO, CaO, and BaO may interact with platinum to form strong intermetallics and thus limit the region of applicability of this technique. The stability of the platinum-rich intermetallics containing alkaline earth metals can be easily and accurately measured at lower temperatures using solid-state galvanic cells with fluoride electrolytes. Data on intermetallic compounds of platinum with elements having only *s* bonding electrons are also relevant to the development of theories of alloy formation.

Wengert and Spanoudis[5] have estimated the upper limit to the Gibbs energies of formation of $MgPt_7$, $MgPt_3$, $CaPt_5$, Ca_2Pt_7, $CaPt_2$, $BaPt_5$, and $BaPt_3$ at 1473 K by establishing the feasibility of simple reactions by which these compounds are formed. Rezukhina and Dmitrieba[6] have measured the Gibbs energies of formation of $BaPt_5$ and $BaPt_2$ using the cells

$$Y + YF_3/CaF_2/BaPt_5 + Pt + BaF_2 \qquad [I]$$

and

$$Y + YF_3/CaF_2/BaPt_2 + Pt + BaF_2 \qquad [II]$$

in the temperature range of 990 to 1265 K. A partial phase diagram for the Pt-Ba system is shown in Figure 1.[7,8] Since both $BaPt_5$ and $BaPt_2$ are stable, the right-hand electrode of cell [II] is thermodynamically unstable. Platinum cannot coexist with $BaPt_2$. Therefore,

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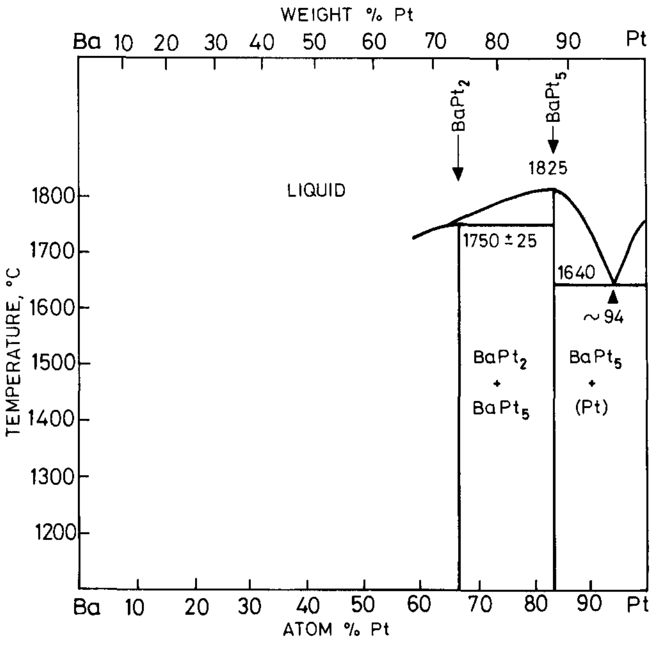

Fig. 1—Partial phase diagram of the system Pt-Ba.[7,8]

the data for $BaPt_2$ require revalidation. Although the mutual solubility between CaF_2 and BaF_2 is expected to be small, a systematic error will result if the activity of BaF_2 is lowered by the formation of a solid solution. In this study, cells have been designed to avoid the presence of the two fluoride phases in contact.

The phase diagram for the Pt-Ca system[8,9,10] shows six stable compounds: $CaPt_5$, Ca_2Pt_7, $CaPt_2$, Ca_3Pt_2, Ca_5Pt_3, and Ca_5Pt_2. The compounds $MgPt_7$, $MgPt_3$, MgPt, Mg_3Pt, and Mg_6Pt have been reported in the Pt-Mg system.[9] There is a lack of quantitative information on thermodynamic properties of intermetallic compounds in the systems Pt-Mg and Pt-Ca.

II. EXPERIMENTAL ASPECTS

A. *Materials*

The platinum metal used in this study was 99.99 pct pure. The metals barium (99.4 pct purity), magnesium (99.9 pct purity), and calcium (99.8 pct purity), supplied by the former Dominion Magnesium Ltd., Haley, Canada, were redistilled before use. The main impurities in barium were calcium (0.25 pct), strontium (0.24 pct), and magnesium (0.7 pct). Similarly, the major impurities in magnesium and calcium were the other Group IIA elements. The metallic compounds were prepared by reacting platinum powder with magnesium at 900 K, calcium at 1100 K, and barium at 990 K in closed crucibles made of iron. The formation of the intermetallics was confirmed by X-ray diffraction and chemical analysis. The contamination of the intermetallics by iron was below analytical limits of detection. The alkaline earth fluoride solid electrolytes were in the form of transparent single crystals. The single crystals and powders of alkaline earth fluorides were of high purity (99.99 pct). PURATRONIC*-grade fine powders of Ni and NiF_2 w obtained from Johnson Matthey Chemicals. Argon g used as an inert atmosphere over the emf cell, v 99.99 pct pure. It was further dried by passage thro magnesium perchlorate and deoxidized by passage thro copper at 700 K and titanium at 1150 K.

Reference electrode pellets containing an equim mixture of Ni and NiF_2 were compacted in a steel and sintered under argon at 1250 K. The working el trode was prepared by mixing powders of compon metal and/or intermetallics with the corresponding kaline earth fluoride. The mixture was compacted un pressure and sintered at 1250 K under argon.

B. *Apparatus*

The apparatus used in this study for emf measu ments was similar to that described earlier.[11] A sc matic diagram is shown in Figure 2. The electrode pel were spring loaded on either side of a transparent sin crystal MF_2 (M = Mg, Ca, Ba). The pellets were h together under pressure through a system consisting springs, an alumina rod, and a flat-bottomed alum tube with a section cut away parallel to its axis, as sho in Figure 2. The electrical connections to the electro were made with platinum wire. Stainless steel sheet wrapped around the outer alumina tube housing the c and the entire assembly was supported inside a verti furnace. The steel sheet was grounded to minimize duced emf on the platinum leads. The cell was ma tained under flowing argon gas at a pressure of 1.

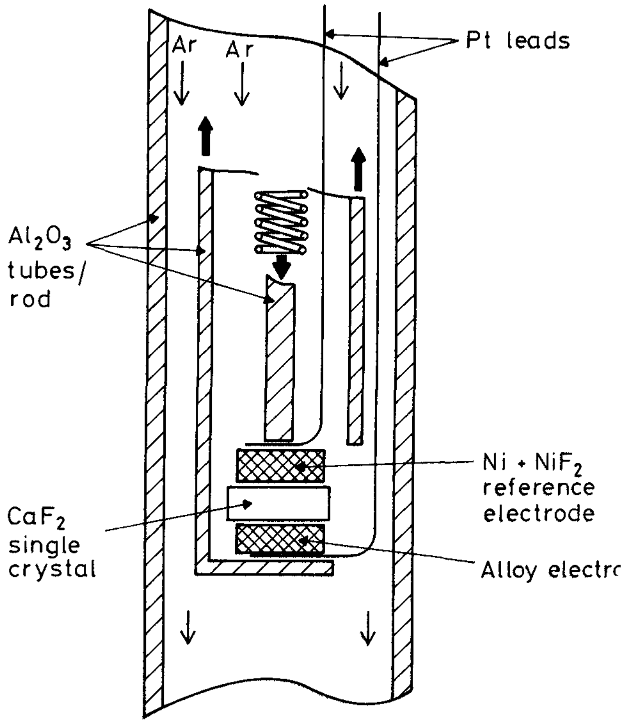

Fig. 2—Schematic diagram of the cell assembly.

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*PURATRONIC is a trademark of Johnson Matthey Plc., Roys England.

10^5 Pa. The temperature of the furnace was controlled to ±1 K and was measured by a Pt/Pt-13 pct Rh thermocouple.

The emf of the following cells was measured as a function of temperature using a high-impedance digital voltmeter:

Pt, Pt + $MgPt_7$ + MgF_2/MgF_2/Ni + NiF_2, Pt [III]

Pt, $MgPt_7$ + $MgPt_3$ + MgF_2/MgF_2/Ni + NiF_2, Pt [IV]

Pt, Pt + $CaPt_5$ + CaF_2/CaF_2/Ni + NiF_2, Pt [V]

Pt, $CaPt_5$ + Ca_2Pt_7 + CaF_2/CaF_2/Ni + NiF_2, Pt [VI]

Pt, Ca_2Pt_7 + $CaPt_2$ + CaF_2/CaF_2/Ni + NiF_2, Pt [VII]

Pt, Pt + $BaPt_5$ + BaF_2/BaF_2/Ni + NiF_2, Pt [VIII]

Pt, $BaPt_5$ + $BaPt_2$ + BaF_2/BaF_2/Ni + NiF_2, Pt [IX]

The cells are written such that the right-hand electrode is positive. Pure MgF_2, CaF_2, and BaF_2 are known to be ionic conductors with ionic transference greater than 0.99 at fluorine potentials encountered in the study.

The emfs of the cells became steady in 2 to 8 hours after the attainment of thermal equilibrium, depending upon the temperature of the cell. The emf was independent (±2 mV) of the flow rate of argon gas through the alumina tube in the range of 1.5 to 5 ml s^{-1}. The reversibility of the cells was checked by microcoulometric titration in both directions. In each case, the cell emf returned to its original value before titration within 30 minutes. This demonstrates that the chemical potential of fluorine at the electrodes returned to the same value after infinitesimal displacement from equilibrium to lower and higher values. The emf was reproducible on repeated temperature cycling. At the end of each experiment, the cell was cooled, and the electrodes were examined by X-ray diffraction. No change in the phase composition of the electrodes during the emf measurement could be detected.

III. RESULTS

The reversible emfs of cells [III] through [IX] are plotted as a function of temperature in Figures 3 through 5. The numbers on each plot indicate the sequence of measurement of emf. The emf is found to vary linearly with temperature. The least-mean squares regression analysis gives the following equations for the emf:

$$E_{\mathrm{III}} = 1110\,(\pm 5) - 0.030\,(\pm 0.005)T \text{ mV} \quad [1]$$

$$E_{\mathrm{IV}} = 1461\,(\pm 9) - 0.083\,(\pm 0.009)T \text{ mV} \quad [2]$$

$$E_{\mathrm{V}} = 1378\,(\pm 6) + 0.035\,(\pm 0.006)T \text{ mV} \quad [3]$$

$$E_{\mathrm{VI}} = 1752\,(\pm 4) + 0.003\,(\pm 0.003)T \text{ mV} \quad [4]$$

$$E_{\mathrm{VII}} = 1861\,(\pm 4) + 0.004\,(\pm 0.003)T \text{ mV} \quad [5]$$

$$E_{\mathrm{VIII}} = 1656\,(\pm 10) - 0.015\,(\pm 0.009)T \text{ mV} \quad [6]$$

$$E_{\mathrm{IX}} = 2014\,(\pm 10) - 0.050\,(\pm 0.010)T \text{ mV} \quad [7]$$

The virtual cell reactions and the corresponding changes in standard Gibbs energies calculated from the emf are listed in Table I. The standard Gibbs energies of for-

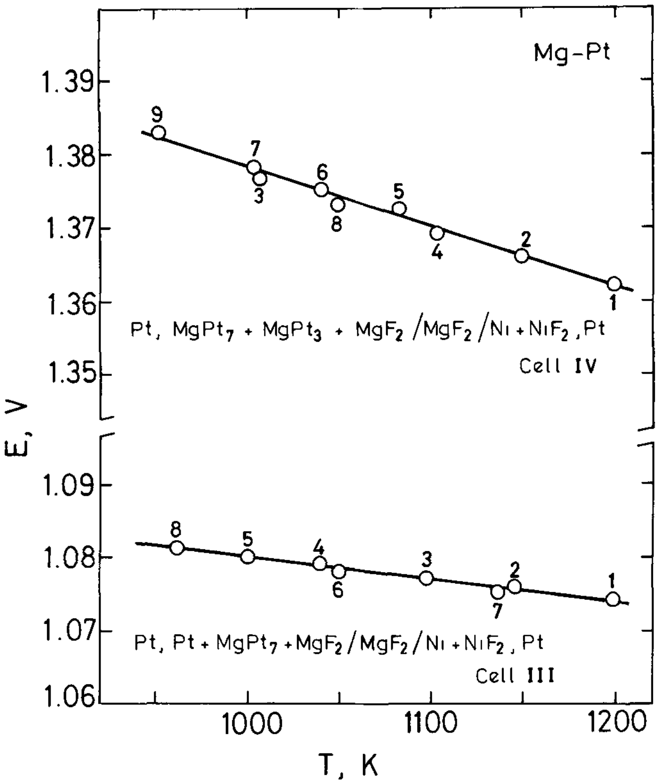

Fig. 3 — Variation of the emf of cells [III] and [IV] with temperature.

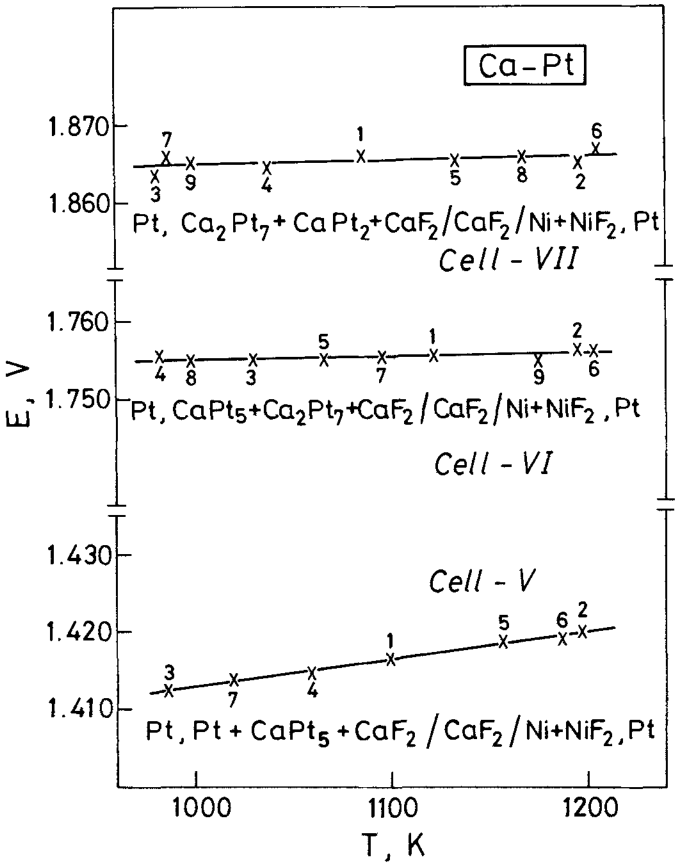

Fig. 4 — Temperature dependence of the emf of cells [V] through [VII].

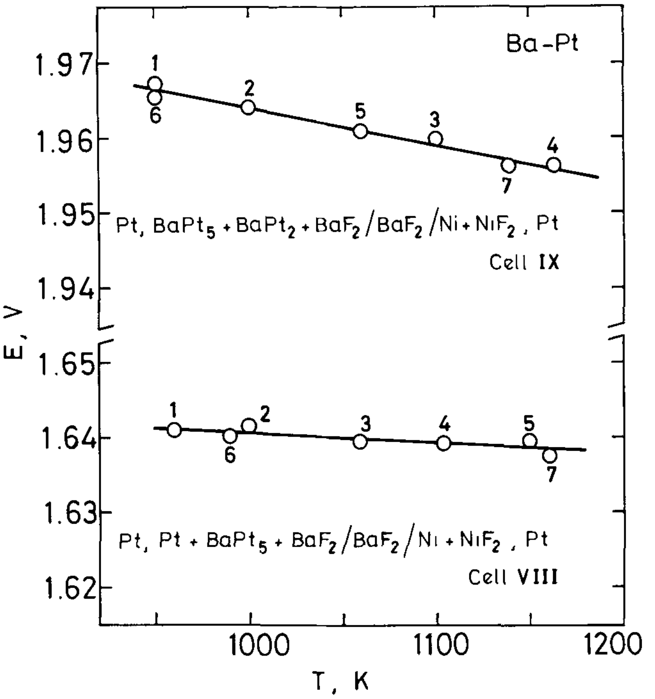

Fig. 5—Temperature dependence of the emf of cells [VIII] and [IX].

mation of the intermetallic compounds of platinum with respect to solid platinum and liquid alkaline earth elements as standard states, derived from the Gibbs energies of cell reactions and Gibbs energies of formation of NiF_2 and MF_2 (M = Mg, Ca, Ba),[12] are given in Table II. The auxiliary thermodynamic data used in the calculations are summarized in Table III. All of the alkaline earth metals (Mg, Ca, and Ba) interact strongly with platinum. Among the three elements, calcium interacts most strongly. The standard Gibbs energies of formation of the intermetallic compounds exhibit only a weak dependence on temperature. The integral Gibbs energies of mixing for the systems Pt-Mg, Pt-Ca, and Pt-Ba at 1100 K are plotted as a function of composition in Figure 6. The relative partial Gibbs energies of mixing of alkaline earth elements corresponding to the two-phase fields are given as a function of temperature in Table IV. The variation of partial free energies as a function of composition at 1100 K and the extrapolated values at 1900 K are displayed in Figure 7. The three systems studied in this work are similar, but the similarities are not as marked as might be expected. Similar compounds, $CaPt_5$ and $BaPt_5$ ($CaCu_5$ type, hP6, P6/mmm) and $CaPt_2$ and $BaPt_2$ ($MgCu_2$ type, cF24, Fd3m), are found in the Pt-Ca and Pt-Ba syste but a compound corresponding to the stoichiometry Ca is not seen in the Pt-Ba phase diagram. In the Pt- system, two cubic superlattice phases, $MgPt_7$ [cP32 and $MgPt_3$ ($AuCu_3$ type, cP4, Pm3m), are seen. Sim structures are not present in Pt-Ca and Pt-Ba system

Table II. Standard Gibbs Energies of Formation Intermetallic Compounds of Platinum with Magnesiu Calcium, and Barium with Respect to Solid Platinu and Liquid Alkaline Earth Metals as Standard State

Compound	ΔG_f° (J/mol)	Temperatu Range (K
$MgPt_7$	$-256{,}100 + 16.5T$ (±2000)	950 to 12
$MgPt_3$	$-217{,}400 + 10.7T$ (±2000)	950 to 12
$CaPt_5$	$-297{,}500 + 13.0T$ (±5000)	975 to 12
Ca_2Pt_7	$-551{,}800 + 22.3T$ (±5000)	975 to 12
$CaPt_2$	$-245{,}300 + 9.3T$ (±5000)	975 to 12
$BaPt_5$	$-238{,}700 + 8.1T$ (±4000)	950 to 11
$BaPt_2$	$-197{,}400 + 4.0T$ (±4000)	950 to 11

IV. COMPARISON WITH THE LITERATU

The upper limits given by Wengert and Spanou for the Gibbs energies of formation of $MgPt_7$, Mg $CaPt_5$, Ca_2Pt_7, $CaPt_2$, and $BaPt_5$ are consistent with results obtained in this study. Wengert and Spanou have estimated the upper bound for the compound Ba but no evidence for this compound was found in study. In agreement with the phase diagram of Savit *et al.*,[7] a Laves phase $BaPt_2$ with a = 9.70 Å was fo in the present study. For all compounds, the actual ues for the Gibbs energies of formation obtained in present study supersede the upper limits estimated Wengert and Spanoudis, based on indirect evidence

The Gibbs energies of formation of $BaPt_5$ and B obtained in the study are in reasonable agreement the data reported by Rezukhina and Dmitrieba,[6] as sh in Figure 8. However, the difference between the Gi energies of formation of $BaPt_5$ and $BaPt_2$ obtained in study is significantly larger than that reported Rezukhina and Dmitrieba.[6] This is probably becaus the unstable mixture of Pt + $BaPt_2$ used as an electr by Rezukhina and Dmitrieba.[6] It would be intere to measure the heat capacity and enthalpy of forma of the intermetallics of platinum with alkaline earth m als so that a more complete thermodynamic descrip can be given.

Table I. Standard Gibbs Energy Change Associated with the Virtual Cell Reaction

Cell	Virtual Cell Reaction	ΔG° (J)
[III]	$NiF_2 + MgPt_7 \rightarrow Ni + 7Pt + MgF_2$	$-214{,}200 + 5.79T$
[IV]	$4NiF_2 + 7MgPt_3 \rightarrow 4Ni + 3MgPt_7 + 4MgF_2$	$-1{,}127{,}900 + 64.07T$
[V]	$NiF_2 + CaPt_5 \rightarrow Ni + 5Pt + CaF_2$	$-266{,}100 - 6.75T$
[VI]	$3NiF_2 + 5Ca_2Pt_7 \rightarrow 3Ni + 7CaPt_5 + 3CaF_2$	$-1{,}014{,}400 - 1.74T$
[VII]	$3NiF_2 + 7CaPt_2 \rightarrow 3Ni + 2Ca_2Pt_7 + 3CaF_2$	$-1{,}077{,}500 - 2.38T$
[VIII]	$NiF_2 + BaPt_5 \rightarrow Ni + 5Pt + BaF_2$	$-319{,}600 + 2.89T$
[IX]	$3NiF_2 + 5BaPt_2 \rightarrow 3Ni + 2BaPt_5 + 3BaF_2$	$-1{,}165{,}500 + 28.95T$

Table III. Auxiliary Thermodynamic Data Used in Calculations

Compound	ΔG_f° (J/mol)	Reference
NiF_2	$-\ 653{,}500 + 151.29T$	12
MgF_2	$-1{,}123{,}780 + 173.59T^*$	12
CaF_2	$-1{,}217{,}100 + 157.53T^*$	12
BaF_2	$-1{,}211{,}790 + 162.28T^*$	12

*With respect to liquid alkaline earth metals and gaseous diatomic fluorine as standard states.

V. SOME APPLICATIONS

High-purity alkaline earth metals can be prepared by the reduction of their very stable oxides by hydrogen in the presence of platinum and their subsequent vaporization from the alloy and condensation onto a desired substrate. Based on the data obtained in this study for the intermetallics and the thermodynamic data available in the literature[13,14] on oxides, an Ellingham diagram can be constructed (Figure 9), showing the oxygen potentials corresponding to the coexistence of the intermetallics with their corresponding oxides as a function of temperature. Lines for the oxygen potentials corresponding to Fe + FeO, Cr + Cr_2O_3, Si + SiO_2, Ba + BaO, Mg + MgO, and Ca + CaO equilibria are also shown in Figure 9 for comparison. A nomographic scale for reading off the equilibrium (P_{H_2}/P_{H_2O}) ratio is also provided. It is seen that the oxygen potentials for the reduction of MgO, CaO, and BaO to form the platinum-rich intermetallics ($MgPt_7$, $CaPt_5$, and $BaPt_5$) lie in a band approximately 50 kJ mol^{-1} below that for the reduction of "FeO." The corresponding equilibrium (P_{H_2}/P_{H_2O})

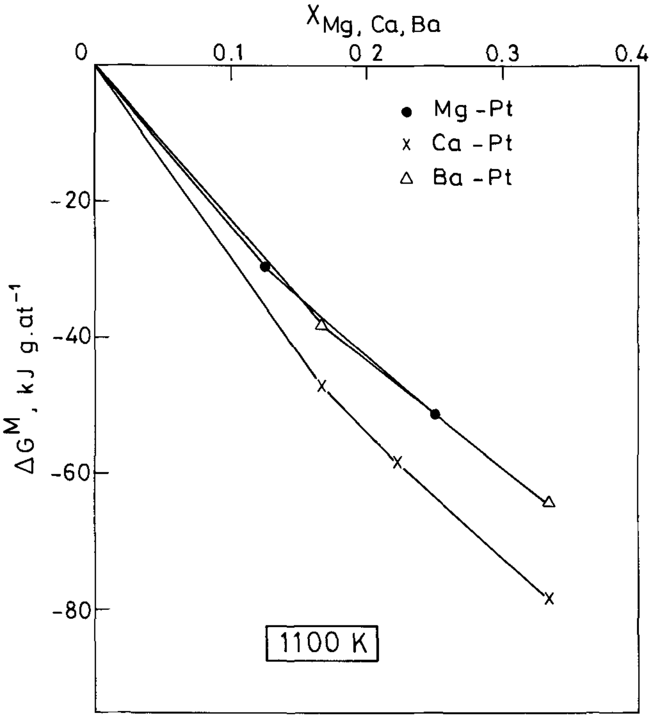

Fig. 6—Composition dependence of the integral Gibbs energy of mixing at 1100 K for the systems Pt-Mg, Pt-Ca, and Pt-Ba.

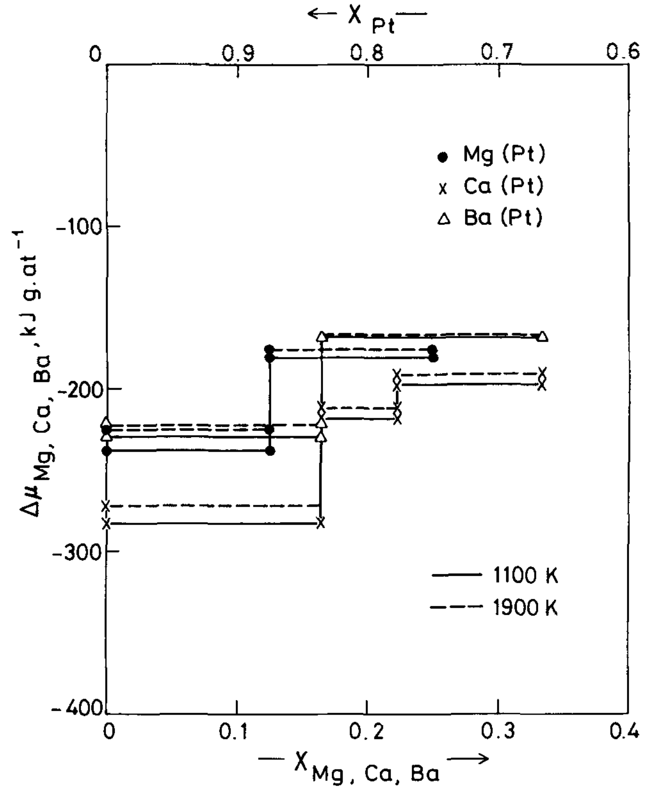

Fig. 7—Variation of the relative partial Gibbs energy of the alkaline earth metals with composition in the systems Pt-Mg, Pt-Ca, and Pt-Ba at 1100 K (measured) and 1900 K (extrapolated) relative to pure liquid standard states.

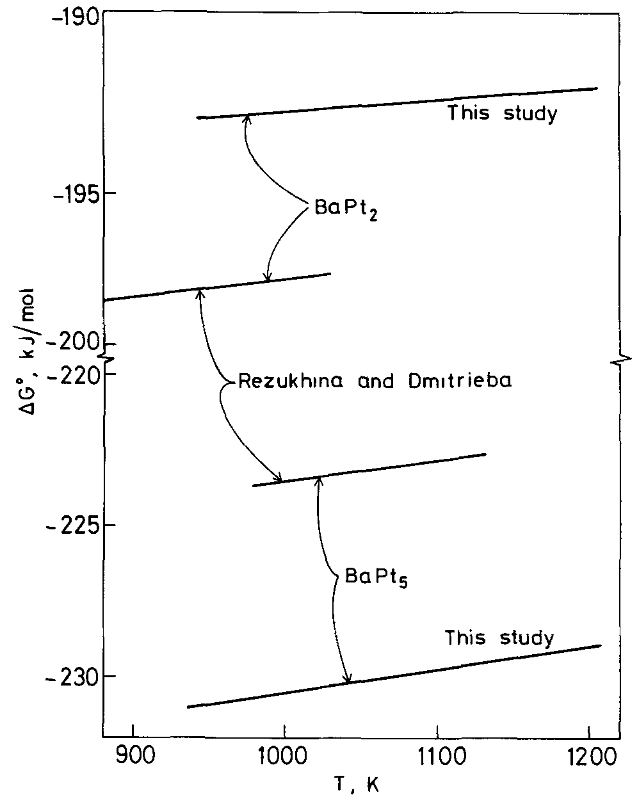

Fig. 8—Comparison of the Gibbs energies of formation of $BaPt_5$ and $BaPt_2$ obtained in this study with the data reported by Rezukhina and Dmitrieba.[6]

Table IV. Relative Partial Gibbs Energies of Alkaline Earth Metals in Two-Phase Fields relative to Liquid Alkaline Earth Metals as Standard States

Phase Mixture	$\Delta G_{\mathrm{Mg,Ca,Ba}}$ (J/mol)
$\mathrm{Pt} + \mathrm{MgPt_7}$	$-256{,}100 + 16.5T$
$\mathrm{MgPt_7} + \mathrm{MgPt_3}$	$-188{,}400 + 6.3T$
$\mathrm{Pt} + \mathrm{CaPt_5}$	$-297{,}500 + 13.0T$
$\mathrm{CaPt_5} + \mathrm{Ca_2Pt_7}$	$-225{,}300 + 6.7T$
$\mathrm{Ca_2Pt_7} + \mathrm{CaPt_2}$	$-204{,}600 + 6.9T$
$\mathrm{Pt} + \mathrm{BaPt_5}$	$-238{,}700 + 8.1T$
$\mathrm{BaPt_5} + \mathrm{BaPt_2}$	$-169{,}700 + 1.3T$

ratios vary from 2 to 80, depending on the element and the temperature. For producing the next intermetallic phase ($MgPt_3$, Ca_2Pt_7, and $BaPt_2$), the equilibrium (P_{H_2}/P_{H_2O}) ratios vary from 70 to 140 in the temperature range of 1300 to 1900 K. A recirculating gas system from which water vapor can be removed by condensation is ideal for carrying out the reduction up to a P_{H_2}/P_{H_2O} ratio of 100. Ammonia may also be used as a reducing agent. The reduction of alkaline earth oxides to form intermetallics richer in alkaline earth elements is less effective from the point of view of the utilization of the reductant hydrogen. Preliminary experiments indicate that the kinetics of reduction are favorable at temperatures above 1450 K.[15] Alkaline earth metals can be recovered from the intermetallic compounds $MgPt_3$, Ca_2Pt_7, and $BaPt_2$ by distillation at temperatures ranging from 1950 2400 K. Much higher temperatures are needed to c compose the platinum-rich intermetallics. The platinu rich intermetallics regenerated after distillation of t alkaline earth metals from $MgPt_3$, Ca_2Pt_7, and Ba can be used for further reduction:

$$3MgPt_7 + 4MgO + 4H_2 \rightarrow 7MgPt_3 + 4H_2O$$

$$7CaPt_5 + 3CaO + 3H_2 \rightarrow 5Ca_2Pt_7 + 3H_2O$$

$$2BaPt_5 + 3BaO + 3H_2 \rightarrow 5BaPt_2 + 3H_2O \quad [1$$

The economics of this process require further study comparison with those based on fused salt electroly and the Pidgeon process.

The high stability of the intermetallic compounds p cludes the use of platinum in contact with alkaline ea oxides at temperatures above 1300 K under reduci conditions. Such contacts are usually encountered in t use of Pt/Pt-Rh thermocouples, platinum electrodes a leads in galvanic cells.

The platinum-slag-gas equilibrium technique has be extensively used for the measurement of the activities FeO, MnO, and Cr_2O_3 in slags. The results of this stuc extrapolated to higher temperatures, may be used for evaluation of the technique for slags containing Mg CaO, and BaO. The Ellingham diagram (Figure 9) sho that the oxygen potentials for the reduction of these c ides to form intermetallics lie between the lines for Fe "FeO" and Si + SiO_2. The platinum-slag-gas equil rium technique is therefore suitable for the study of tivities of FeO, MnO, and Cr_2O_3 in slags containing Mg CaO, and BaO provided the oxygen potential of the phase is maintained well above that corresponding to Fe + "FeO" equilibrium.

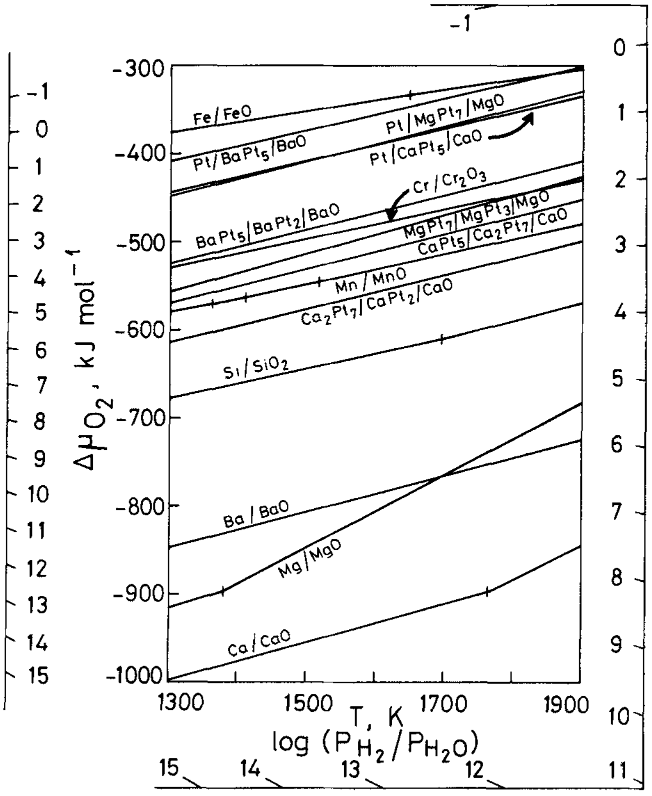

Fig. 9—Ellingham diagram for oxides, showing the temperature dependence of oxygen potentials for the coexistence of intermetallics of platinum with alkaline earth metals with their corresponding oxides. Nomographic scale for reading off the P_{H_2}/P_{H_2O} ratio is provided.

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