(5) Widom, B. *Phys. Rev. Lett.* **1975**, *34*, 999.
(6) Francis, A. W. "Liquid-Liquid Equilibriums"; Interscience: New York, 1963; p 286.
(7) Fleming, P. D.; Vinatieri, J. E. *AIChE J.* **1979**, *25*, 493.
(8) Hubbard, J.; Schofield, P. *Phys. Lett. A* **1972**, *40*, 245.
(9) Fleming, P. D. *J. Colloid Interface Sci.* **1978**, *65*, 46.
(10) Widom, B. *J. Chem. Phys.* **1965**, *43*, 3892 and in "Phase Transitions and Critical Phenomena"; Domb, C., Green, M. S., Eds., Academic Press: New York, 1972.
(11) Boneau, D. F.; Clampitt, R. L. *J. Pet. Technol.* **1977**, *29*, 501.
(12) Healy, R. N.; Reed, R. L. *Soc. Pet. Eng. J.* **1977**, *17*, 129.
(13) Widom, B. "The Interface between Fluid Phases"; paper Coll 089, presented at the 179th ACS National Meeting, Houston, TX, March 23-28, 1980.
(14) Widom, B. *J. Phys. Chem.* **1973**, *77*, 2196.

Received for review January 31, 1980. Accepted December 2, 1980.

Critical Evaluation of Thermodynamic Properties of Mixing for Solid Cobalt-Platinum Alloys between 1000 and 1400 K

Jean Pierre Cyr, Jacques Dellacherie, and Daniel Balesdent*

Ecole Nationale Superieure des Industries Chimiques, Institut National Polytechnique de Lorraine, 54042 Nancy Cedex, France

The most recent compilation of the thermodynamic properties of mixing for cobalt-platinum alloys was published in 1973 by Hultgren et al. but does not include all of the experimental results now available, particularly Miner's; moreover, Hultgren's tables present only the Gibbs energy of components, without enthalpy or entropy data. We have made a new critical evaluation that leads to the best values of total and partial enthalpy, entropy, and Gibbs energy of cobalt and platinum, in solid alloys, in the temperature range 1000-1400 K. These results are presented in three tables and shown in several figures.

1. Introduction

We have determined the thermodynamic properties of stoichiometric defects in cobalt oxide by means of measurements of the electronic conductivity as a function of composition, the latter being imposed by contacting the oxide with a cobalt-platinum alloy. To be able to use these conductivity measurements, we require, in addition to other data, thermodynamic data of mixing for cobalt-platinum alloys. The most recent compilation, published in 1973 by Hultgren et al. (*1*), does not include all of the experimental results now available; moreover, Hultgren's tables present only the Gibbs energy of components, without enthalpy or entropy data. This paper reports the results of the critical evaluation we have been led to make, for total and partial Gibbs energy, enthalpy, and entropy of components.

2. History

The first activity measurements on solid cobalt-platinum alloys were made by Orlani (*2*) in 1953. By measuring the emf of cells having a molten LiCl-KCl eutectic as electrolyte and working between 973 and 1173 K, he found a negative deviation for cobalt activities and a positive deviation for those of platinum. In addition he found positive enthalpies of mixing, which is in complete disagreement with all further measurements, notably those he carried out with Murphy (*3*) in 1962, using differential calorimetry for the dissolution of liquid tin at ~913 K. They found a total molar enthalpy of mixing ΔH^M of -9500 J mol^{-1} at $x_{Co} = 0.3$ and -1690 J mol^{-1} at $x_{Co} = 0.153$ for disordered alloys of cobalt-platinum. The values published in cal mol^{-1} have been converted to J mol^{-1} on the basis of 1 cal = 4.184 J.

Rudman and Averbach (*4*), using X-ray measurements of the short-distance order parameters for Co-Pt alloys and assuming a quasi-chemical model of the interaction between the closest neighbors, calculate the total molar enthalpies of mixing to fit the expression $\Delta H^M = Ax_{Co}x_{Pt}$ in which $A = -(35600 \pm 1300)$ J mol^{-1}. If such an expression were developed from the measurements of Orlani and Murphy (*3*), the value of A would be -44 800 J mol^{-1}.

In 1964 Schwerdtfeger and Muan (*5*) measured the activity of cobalt in Co-Pt alloys at 1473, 1573, and 1673 K, with compositions ranging from 3 to 100 at. % of cobalt of two complementary techniques: (1) A sample of a Co-Pt alloy was suspended in a thermobalance under a partial pressure of oxygen which was slowly increased by small increments until the alloy was oxidized and its weight increased. (2) A mixture of Co-Pt alloy and the oxide CoO was maintained at equilibrium at a constant temperature under a fixed partial pressure of oxygen; then the temperature was brought rapidly to ambient temperature and the composition of the alloy was determined.

King (*6*) and Miner (*7*) measured the activities of solid cobalt-platinum alloys from 10 to 90 at. % cobalt and temperature between 1073 and 1273 K for King and between 1173 and 1473 K for Miner. They both used solid electrolyte cells which may be schematized by the following: $|Pt,air|(ZrO_2)_{0.85}(CaO)_{0.15}|Co\text{-}Pt,CoO|$ for King (*6*); $|Co,CoO|(ThO_2)_{0.85}(Y_2O_3)_{0.15}|Co\text{-}Pt,CoO|$ for Miner (*7*).

These cells differ not only by the solid electrolyte used (zirconia stabilized with CaO or thoria stabilized with yttrium oxide) and by the partial pressure of oxygen used as reference (air or Co-CoO equilibrium mixture) but also in the way they were constructed, which will be dealt with later.

In 1966 Winters (*8*) used the Knudsen effusion technique to determine the vapor pressure of cobalt above six Co-Pt alloys at composition from 50 to 100 at. % cobalt at 1693 K. The thermodynamic mixing data for the Co-Pt solution at atomic fractions of Co less than 0.5 have been obtained by extrapolation. The total Gibbs energy of mixing ΔG^M goes through a minimum at -1700 J mol^{-1} for $x_{Co} = 0.55$. This same Knudsen effusion technique was used by Alcock and Kubik (*9*) in 1968 to measure the activities of cobalt in liquid Co-Pt alloys from 40 to 80 at. % cobalt at 1823-1923 K; it was also used in 1978 for the same purpose by Chegodaev et al. (*10*).

Smith and Masson also give cobalt activity in Co-Pt-Rh alloy (*11*), by equilibrating the alloys with cobalt oxide and oxygen of known pressure.

Other work was done on this alloy, especially with regard to low-temperature specific heat for studies of magnetic anomalies (*12*, *13*). Phase diagrams with ordered solids were also studied.

0021-9568/81/1726-0174$01.25/0

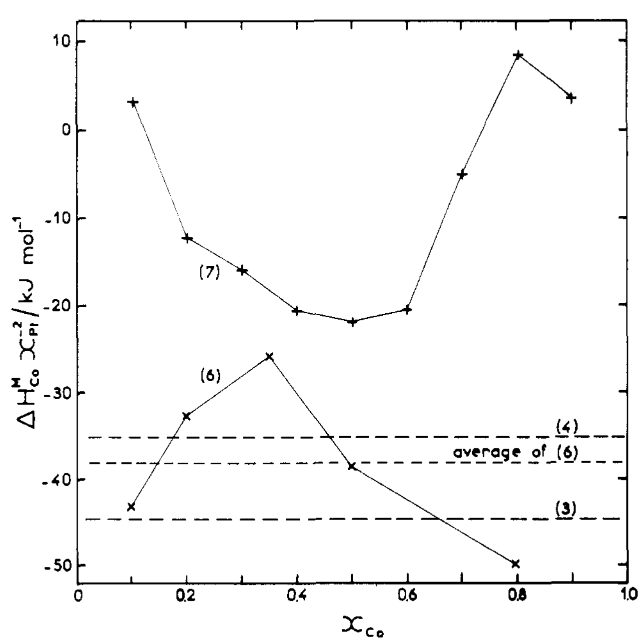

Figure 1. Comparison of the values of the function $\Delta H_{Co}^M/x_{Pt}^2$ calculated from the results of Orlani and Murphy (*3*, calorimetry), Rudman and Averbach (*4*, calculation), King (*6*, emf), and Miner (*7*, emf).

This brief bibliography indicates that the only relatively complete measurements on solid Co–Pt alloys in the temperature range 1000–1400 K are those of King (*6*) and Miner (*7*). Miner does not mention King's results. Only King's results were used in Hultgren's 1973 compilation (*1*), where Miners's thesis is only mentioned in additional references. Moreover Hultgren's compilation presents only Gibbs energy of mixing without mention of enthalpy or entropy data.

We therefore intend to compare the results of the workers to find whether they are compatible with one other, with themselves, and with the measurements made by the other authors mentioned. This critical and comparative appraisal should allow us to select the most reliable results from which we may determine thermodynamic data of mixing for cobalt–platinum alloys between 1000 and 1400 K (total and partial Gibbs energies, enthalpies, and entropies of the components).

3. Comparison and Discussion of the Results of the Workers

The emf E of the cell used by Miner gives directly the cobalt partial Gibbs energy of mixing by $\Delta G_{Co}^M = -2EF$, where $F = 96\,484.56$ C mol^{-1} is the Faraday constant.

On the other hand, King took the electrode (Pt,air) as a reference, so that the experimental emf E leads to ΔG_{Co}^M by $\Delta G_{Co}^M = -2F(E_0 - E)$, where E_0 is the measured emf of the cell when the electrode (CoO,alloy) is in point of fact made of CoO and pure cobalt.

The emf measurements of King and Miner were made at various temperatures for each of their alloys; therefore the partial molar entropies and enthalpies of mixing and excess can be obtained by linear regression from the experimental values of $\Delta G_{Co}^M(T) = \Delta H_{Co}^M - T\Delta S_{Co}^M$. Excess entropy is obtained by $\Delta S_{Co}^E = \Delta S_{Co}^M + R \ln x_{Co}$, where $R = 8.31441$ J K^{-1} mol^{-1} is the perfect gas constant.

The values $\Delta H_{Co}^M/x_{Pt}^2$ and $\Delta S_{Co}^E/x_{Pt}^2$ calculated in this way from measurements of King and of Miner are shown in Figures 1 and 2. It can be seen that there is a rough agreement for the entropies but complete disagreement for the enthalpies. The dotted lines show the two horizontal lines corresponding to

$$\Delta H_{Co}^M/x_{Pt}^2 = -38440 \text{ J mol}^{-1}$$

$$\Delta S_{Co}^E/x_{Pt}^2 = +8.74 \text{ J K}^{-1} \text{ mol}^{-1}$$

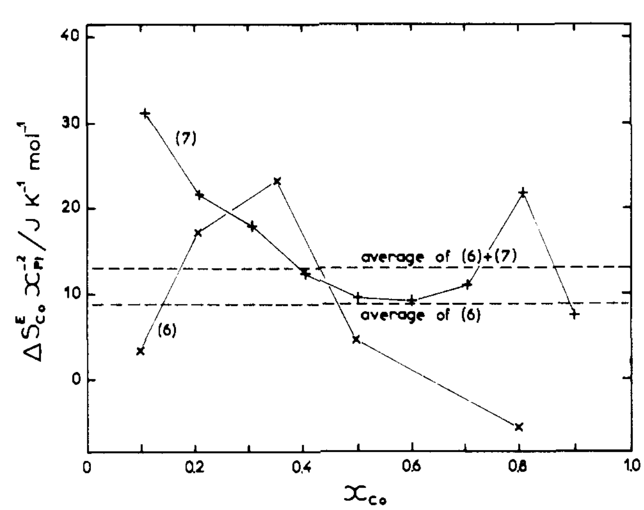

Figure 2. Comparison of the values of $\Delta S_{Co}^E/x_{Pt}^2$ calculated from the measurements of King (*6*, emf) and Miner (*7*, emf).

These values are taken from the expression for the total molar excess Gibbs energy ΔG^E

$$\Delta G^E/(\text{cal mol}^{-1}) = (-9188 - 2.09T/\text{K})x_{Co}x_{Pt}$$

proposed by King to account for these results.

We have also marked the following values on Figure 1 in dotted lines: $\Delta H_{Co}^M/x_{Pt}^2 = -35600$ J mol^{-1}, calculated by Rudman and Averbach (*4*), and $\Delta H_{Co}^M/x_{Pt}^2 = -44800$ J mol^{-1}, calculated from the differential calorimetric measurements of Orlani and Murphy (*3*). It may be seen that King's measurements are in accord with those of Rudman and Averbach and those of Orlani and Murphy, but not at all with those of Miner, who obtains enthalpies which are much too high.

We will now compare King's and Miner's results with those of Schwerdtfeger and Muan (*5*). These workers measured the oxygen pressures at the equilibrium of CoO with either pure cobalt or cobalt in platinum alloys between 1473 and 1573 K. However, as they themselves recognized, the dispersion of their results is too great to allow values of ΔH_{Co}^M and ΔS_{Co}^E to be obtained by ΔG_{Co}^M as a function of temperature. The various values of $\Delta G_{Co}^E/x_{Pt}^2$ are shown in Figure 3. Here again, it can be seen that it is King's results and not Miner's which are compatible with the results of Schwerdtfeger and Muan, the values of ΔG_{Co}^E found by Miner being too high.

Finally, we include Winter's (*8*) results at 1963 K; these, however, give values for the total Gibbs energy of mixing, which are much too negative. When King's results are extrapolated to 1963 K, we find a value of −23 000 J mol^{-1} for $x_{Co} = 0.55$, and Winter's value is −34700 J mol^{-1}.

We may conclude that the measurements made by King are to be prefered over those of Miner, who finds Gibbs energies of mixing which are consistently too high. The reason for this systematic error is to be found in the technique used. King compressed a large quantity of a mixture of powdered Co–Pt alloy and CoO oxide at the bottom of a stabilized zirconia sheath, 30 cm long and made by Zircoa (Zirconium Corp. of America, USA). The outside end of this sheath was platinized and swept by a flow of air. There is therefore no possible contact between the two atmospheres inside and outside the sheath. On the other hand, Miner used (Co–Pt,CoO) and (Co,CoO) electrodes in the form of pellets (1.6 mm thick and 3 mm in diameter) compressed with a disk (1.6 mm thick and 5 mm in diameter) of thoria stabilized with yttrium oxide which he prepared himself from high-purity materials. This cell was incorporated in a set of tubes and sheaths of alumina or mullite swept by a flow of purified argon. Thus, the atmospheres of the two electrodes are not isolated. Very small amounts, even only traces, of reducing or oxidizing agents as impurities (such

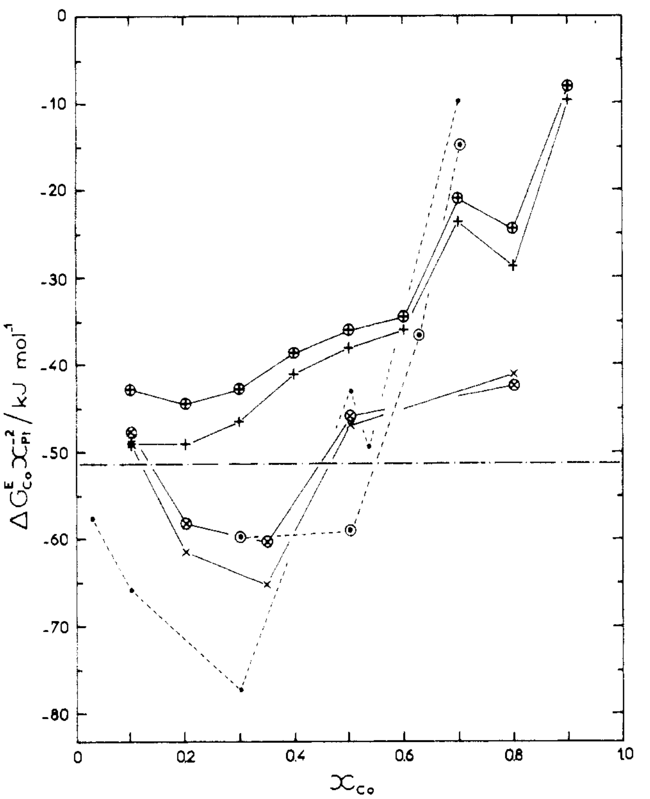

Figure 3. Comparison of the values of $\Delta G_{Co}^E/x_{Pt}^2$ calculated from the results of Schwerdtfeger and Muan (*5*, thermogravimetry at (⊙) 1200 and (●) 1400 °C), extrapolated from the results of King (*6*, emf at (⊗) 1200 and (×) 1400 °C) and of Miner (*7*, emf at (⊕) 1200 and (+) 1400 °C), and tabulated by Hultgren (-·-·).

as H_2, H_2O, CO, or CO_2) in the flow of purified argon sweeping the cell would be sufficient to create a vector to transport oxygen from one electrode to the other. This would tend to reduce the chemical potential between the two electrodes and decreases the emf of the cell. This phenomena would also be amplified by the fact that the quantity of materials in the electrodes is too small. Miner experienced a great number of problems with a drift in the emf which, in addition, varied with the flow rate of argon, and he was obliged to continually modify his operating method to try to solve these problems. His equilibrium emf measurements were obtained by measurements every 5 min, over only ~0.5 h, which is too short a time to be sure of the stability of an emf. All of these reasons explain why Miner measured absolute values of emf which were too small and which therefore led to values of ΔG_{Co}^M which were not negative enough.

King initially used a technique similar to that of Miner but did not manage to obtain reproducible results because of the continual drift of the emf. This led him to abandon the technique and adopt that described above. Only by completely isolating the atmospheres of the two electrodes (Co-Pt,CoO) or (Co,CoO) did he succeed in obtaining stable values of emf. We ourselves have also experienced this sort of problem in our own work with solid electrolyte galvanic cells.

It should be noted that, while the absolute values of the emf measured by Miner are subject to a systematic error, their variation with temperature is not necessarily subject to the same systematic error and can be taken as an independent quantity. Accordingly, the molar entropies of mixing found by Miner should not be systematically rejected, since they are relatively compatible with those calculated from King's results.

To conclude this discussion, it should be noted that Hultgren's compilation gives values of integral and partial Gibbs energy for solid alloys at 1273 K which can be obtained exactly from the relation $\Delta G_{Co}^E(1273\ K)/(cal\ mol^{-1}) = -(11860 \pm 2400)x_{Pt}^2$. With King's value of entropy, the partial excess Gibbs energy of cobalt can be corrected for the temperature difference that leads to a value at 1473 K of $\Delta G_{Co}^E(1473\ K)/x_{Pt}^2 = -(51400 \pm 10000)$ J mol^{-1}. This value is indicated in Figure 3, along with other results.

4. Treatment of King's Experimental Results

King measured the molar Gibbs energy of mixing of cobalt ΔG_{Co}^M at 1073, 1173, 1223, and 1273 K, for the following atomic fractions of cobalt: 0.1000, 0.1998, 0.3498, 0.5000, and 0.7997. He correlated his results with the function

$$\Delta G^E/(cal\ mol^{-1}) = (-8188 - 2.09T/K)x_{Co}x_{Pt}$$

Such a function should lead to values of $\Delta G_{Co}^E/x_{Pt}^2$ which are independent of the atomic fraction x_{Co}. A glance at Figure 3 shows immediately that this is not the case. In addition, the form of the function ΔG^E chosen assumes that the cobalt-platinum solution is symmetrical. This seems to be doubtful because the ordered phases obtained by cooling the disordered solid are CoPt and $CoPt_3$ but never Co_3Pt; this does not help to indicate a symmetrical behavior for the cobalt-platinum solid solution.

We therefore prefer to work on King's raw measurements in the following manner. King made two measurements of emf for each alloy composition and each temperature. Therefore, for each of the five values of x_{Co} we have eight values of ΔG_{Co}^E at 1073, 1173, 1223, and 1273 K, from which we can calculate five values of $\Delta S_{Co}^E/x_{Pt}^2$. The dispersion of points in Figure 2 suggests using a constant value of $\Delta S_{Co}^E/x_{Pt}^2$ of 9 ± 7 J K^{-1} mol^{-1}. We can make the same calculation with Miner's data; the results are given in Figure 2 and are not in great disagreement with the average previous value $\Delta S_{Co}^E/x_{Pt}^2 = 9 \pm 7$ J K^{-1} mol^{-1}.

Thus we can calculate for each experimental measure a value of the function

$$\Delta G_{Co}^E(1173,x_{Co}) = \Delta G_{Co}^E(T,x_{Co}) + (T - 1173)\Delta S_{Co}^E$$

with

$$\Delta S_{Co}^E = (9 \pm 7)x_{Pt}^2\ J\ K^{-1}\ mol^{-1}$$

Thus for each of these values of x_{Co}, we obtain values of $\Delta G_{Co}^E(1173)$ from which we calculate an average value. These average values of $\Delta G_{Co}^E(1173)$ are given in Figure 4 as a function of x_{Co} with a vertical line to show the dispersion about the mean (extremal values).

It would be useful to have a simple polynomial to represent this quantity as a function of x_{Co}. However, as may be seen from the form of the function $\Delta G_{Co}^E(1173)/(1 - x_{Co})^2$ which is plotted in the lower right-hand side of Figure 4, the polynomial would have to be of too high a degree since there are only five points to represent. For this reason, we have used a graphical interpolation of the average values of $\Delta G_{Co}^E(1173,x_{Co})$; thus we can calculate ΔG_{Co}^E for different values of T and different values of x_{Co} by means of the following expression:

$$\Delta G_{Co}^E(T,x_{Co}) = \Delta G_{Co}^E(1173,x_{Co}) - (T - 1173)\Delta S_{Co}^E(x_{Co})$$

with

$$\Delta S_{Co}^E = (9 \pm 7)(1 - x_{Co})^2\ J\ K^{-1}\ mol^{-1}$$

By this method and for each value of x_{Co} in the alloys used by King, we have calculated values for the function ΔG_{Co}^E (calculated) - ΔG_{Co}^E (measured) and present these results in Figure 5. It can be seen that, for a given value of x_{Co}, the results are distributed at random, around a mean value of zero. This may be considered to be a justification of our method of treating King's (*6*) results.

Table I. Partial Molar Quantities of Cobalt for Solid Alloys at 1173 K[a]

x_{Co}	a_{Co}	γ_{Co}	ΔG_{Co}^E/(J mol^{-1})	ΔH_{Co}^M/(J mol^{-1})	ΔS_{Co}^E/(J K^{-1} mol^{-1})
1.0	1.000	1.000	0	0	0
0.9	0.855	0.950	−500 ± 100	−400 ± 200	0.09 ± 0.07
0.8	0.668	0.835	−1 760 ± 300	−1 300 ± 600	0.4 ± 0.3
0.7	0.480	0.686	−3 680 ± 400	−2 700 ± 1100	0.8 ± 0.6
0.6	0.302	0.503	−6 690 ± 500	−5 000 ± 1800	1.4 ± 1.1
0.5	0.160	0.320	−11 100 ± 1000	−8 500 ± 3100	2.3 ± 1.8
0.4	0.064	0.160	−17 900 ± 1600	−14 100 ± 4600	3.2 ± 2.5
0.3	0.018	0.060	−27 500 ± 1800	−22 300 ± 5800	4.4 ± 3.4
0.2	0.006	0.030	−34 100 ± 1800	−27 300 ± 7000	5.8 ± 4.5
0.1	0.002	0.020	−38 200 ± 1700	−29 600 ± 8400	7.3 ± 5.7
0.0	0.000	0.017	−40 000 ± 2100	−29 400 ± 10300	9.0 ± 7.0

[a] $Co_{(s)} = Co(\text{in alloy})_{(s)}$.

Table II. Partial Molar Quantities of Platinum for Solid Alloys at 1173 K[a]

x_{Pt}	a_{Pt}	γ_{Pt}	ΔG_{Pt}^E/(J mol^{-1})	ΔH_{Pt}^M/(J mol^{-1})	ΔS_{Pt}^E/(J K^{-1} mol^{-1})
0.0	0.000	0.009	−46 000 ± 2400	−35 400 ± 10600	9.0 ± 7.0
0.1	0.002	0.021	−37 800 ± 1900	−29 200 ± 8600	7.3 ± 5.7
0.2	0.009	0.044	−30 500 ± 2200	−23 700 ± 7500	5.8 ± 4.5
0.3	0.024	0.079	−24 700 ± 1900	−19 500 ± 5900	4.4 ± 3.4
0.4	0.056	0.140	−19 200 ± 1700	−15 400 ± 4700	3.2 ± 2.5
0.5	0.121	0.243	−13 800 ± 1800	−11 200 ± 3900	2.3 ± 1.8
0.8	0.256	0.426	−8 320 ± 1800	−6 600 ± 3100	1.4 ± 1.1
0.7	0.507	0.725	−3 140 ± 1300	−2 200 ± 2000	0.8 ± 0.6
0.8	0.732	0.916	−860 ± 800	−400 ± 1100	0.4 ± 0.3
0.9	0.889	0.988	−120 ± 300	0 ± 400	0.09 ± 0.07
1.0	1.000	1.000	0 ± 0	0 ± 0	0 ± 0

[a] $Pt_{(s)} = Pt(\text{in alloy})_{(s)}$.

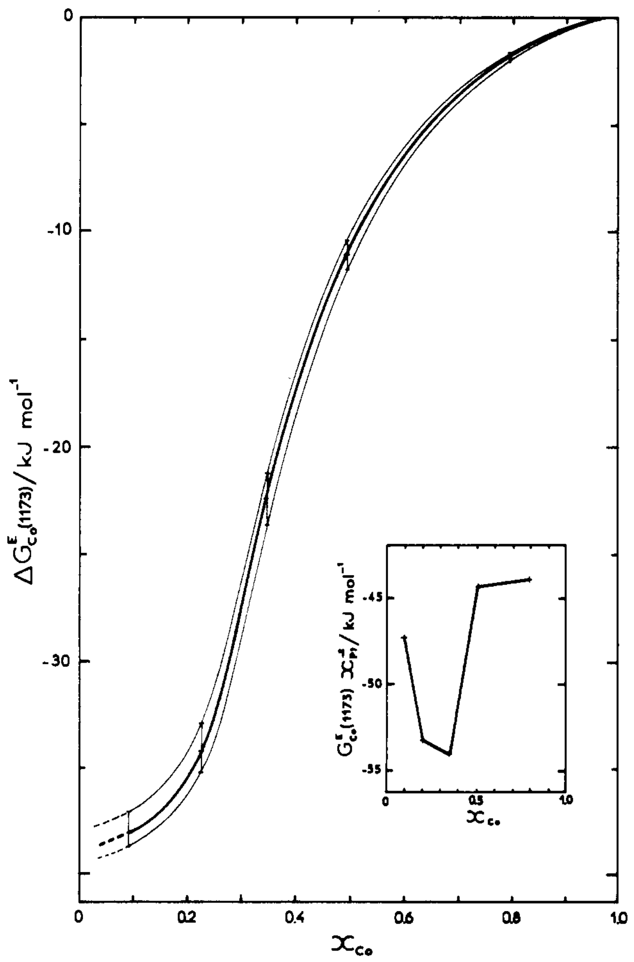

Figure 4. Variations of the function $\Delta G_{Co}^E(1173)$ vs. x_{Co} from the results of King.

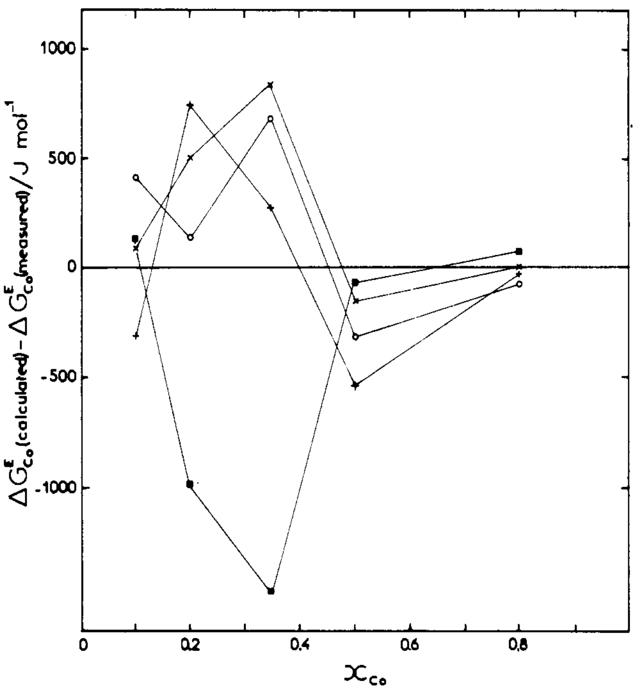

Figure 5. Variation of the difference ΔG_{Co}^E (calculated) − ΔG_{Co}^E (measured) vs. x_{Co} at different temperatures from the results of King (*1*) at (■) 800, (○) 900, (×) 950, and (+) 1000 °C.

5. Thermodynamic Properties of Cobalt–Platinum Alloys

From the graph of the function $\Delta G_{Co}^E(1173)$, we can make a point-by-point calculation of the function $\Delta G_{Co}^E(1173)/x_{Pt}^2$ to make a graphical integration of

$$I(x_{Co}) = \int_0^{x_{Co}} \frac{\Delta G_{Co}^E(1173)}{(1 - x_{Co})^2}\, dx_{Co}$$

Table III. Integral Molar Quantities for Solid Alloys at 1173 K[a]

x_{Pt}	ΔG^E/(J mol^{-1})	ΔH^M/(J mol^{-1})	ΔS^E/(J K^{-1} mol^{-1})
0.0	0 ± 0	0 ± 0	0 ± 0
0.1	−4 230 ± 100	−3300 ± 800	0.8 ± 0.6
0.2	−7 500 ± 200	−5800 ± 1500	1.4 ± 1.1
0.3	−10 000 ± 290	−7800 ± 2000	1.9 ± 1.5
0.4	−11 690 ± 370	−9200 ± 2300	2.2 ± 1.7
0.5	−12 470 ± 430	−9800 ± 2500	2.3 ± 1.8
0.6	−12 160 ± 430	−9600 ± 2400	2.2 ± 1.7
0.7	−10 430 ± 380	−8200 ± 2100	1.9 ± 1.5
0.8	−7 510 ± 300	−5800 ± 1600	1.4 ± 1.1
0.9	−3 930 ± 170	−3000 ± 900	0.8 ± 0.6
1.0	0 ± 0	0 ± 0	0 ± 0

[a] $(1-x)\mathrm{Co}_{(s)} + x\mathrm{Pt}_{(s)} = \mathrm{Co}_{(1-x)}\mathrm{Pt}_{x(s)}$.

and obtain the values of the integral function $\Delta G^E(1173) = (1 - x_{Co})I(x_{Co})$ and the partial function of platinum

$$\Delta G_{Pt}{}^E(1173) = [\Delta G^E(1173) - x_{Co}\Delta G_{Co}{}^E(1173)]/(1 - x_{Co})$$

for various values of the atomic fraction x_{Co}. From this, we obtain γ_{Co}, a_{Co}, γ_{Pt}, and a_{Pt} at 1173 K. The results of these calculations are shown in Tables I and II.

To calculate the mixture properties of cobalt-platinum alloys at any given temperature T between 1000 and 1400 K, we take values of $\Delta G_{Co}{}^E(1173)$ and $\Delta G_{Pt}{}^E(1173)$ from Table I and calculate

$$\Delta G_{Co}{}^E(T,x_{Co}) = \Delta G_{Co}{}^E(1173,x_{Co}) - (T - 1173)\Delta S_{Co}{}^E(x_{Co})$$

with

$$\Delta S_{Co}{}^E(x_{Co}) = (9 \pm 7)(1 - x_{Co})^2 \text{ J K}^{-1} \text{ mol}^{-1}$$

By replacing the subscript Co by Pt, we obtain an analogous expression for platinum.

Finally we may note that the results shown on Tables I and II allow the partial molar enthalpy of mixing of cobalt and platinum between 1000 and 1400 K to be calculated since

$$\Delta H_{Co}{}^M = \Delta H_{Co}{}^E = \Delta G_{Co}{}^E(1173) + 1173\Delta S_{Co}{}^E$$

and a similar expression exists for platinum. The molar integral enthalpy of mixing is very easily obtained since

$$\Delta H^M = x_{Co}\Delta H_{Co}{}^M + x_{Pt}\Delta H_{Pt}{}^M$$

Table III shows the results of these calculations.

We can see that the integral heat of mixing is not very far from the results (*3*, *4*) mentioned in section 2 of this work.

Uncertainties were given for Gibbs energies and for entropies from the experimental dispersion of Miner's results, as explained in section 4. Uncertainties of enthalpies are issued from the relation $H = G + TS$.

6. Conclusion

The results of this critical evaluation are summarized in three tables. Tables I–III give respectively partial quantities of cobalt, partial quantities of platinum, and integral quantities: activities, activity coefficients, excess Gibbs energies, enthalpies of mixing, and excess entropies. These quantities are given at 1173 K but lead to activity and Gibbs energies between 1000 and 1400 K with enthalpies and entropy independent of temperature and Gibbs energy given by $\Delta G = \Delta H - T\Delta S$, for integral and partial quantities.

No new information was obtained from experiments in low-temperature data or in liquid alloys, so that Hultgren's compilation does not need modification in these domains.

Glossary

a_i	activity with respect to solids elements i
emf	electromotive force
ΔG^E	excess molar Gibbs energy
ΔH^M	enthalpy of mixing
R	perfect gas constant (8.31441 J K^{-1} mol^{-1})
ΔS^E	excess molar entropy
T	thermodynamic temperature in Kelvin
x_i	mole fraction of element i

Greek Letters

γ_i	activity coefficient of element i

Subscripts

Co	partial quantities of cobalt
Pt	partial quantities of platinum

Literature Cited

(1) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K. "Selected Values of the Thermodynamic Properties of the Elements" (Vol. 1) and Selected Values of the Thermodynamic Properties of Binary Alloys" (Vol. 2); American Society for Metals: Metals Park, OH, 1973.
(2) Orlani, R. A. *Acta Metall*. **1953**, *1*, 144.
(3) Orlani, R. A.; Murphy, W. K. *Acta Metall*. **1962**, *10*, 879.
(4) Rudman, P. S.; Averbach, B. L. *Acta Metall*. **1957**, *5*, 65.
(5) Schwerdtfeger, K.; Muan, A. *Acta Metall*. **1964**, *12*, 905.
(6) King, R. J. Ph.D. Thesis, University of Pittsburgh, Pittsburgh, PA, 1967.
(7) Miner, R. Ph.D. Thesis, University of Denver, Denver, CO, 1969
(8) Winters, G. R. 1969, Department of Commerce; Clearinghouse Report AD-638421.
(9) Alcock, C. B.; Dubik, A. *Trans.—Inst. Min. Metall., Sect. C* **1968**, *77*, 220.
(10) Chegodaev, A. I.; Dubinin, E. L.; Timofleer, A. I.; Vatolin, N. A. *Zh. Fiz. Khim*. **1978**, *52*, 243.
(11) Smith, I. B.; Masson, C. R. *Can. Metall. Q* **1970**, *9*, 415.
(12) Nieuwenhuys, G. J.; Pikart, M. F.; Zwart, J. J.; Boerstoel, B. M.; Van Den Berg, G. J. *Physica (Utrecht)* **1973**, *69*, 119.
(13) Costa-Ribeiro, P.; Saint-Paul, M.; Thoulouse, D.; Tournier, R. *Low Temp. Phys.—Lt 13, Proc. Int. Conf. Low Temp. Phys., 13th, 1972* **1974**, *2*, 520.

Received for review February 19, 1980. Accepted October 24, 1980.

Excess Thermodynamic Functions for Ternary Systems. 7. Total Pressure Data and G^E for Acetone/1,4-Dioxane/Water at 50 °C

Joseph R. Loehe, Hendrick C. Van Ness,* and Michael M. Abbott*

Chemical and Environmental Engineering Department, Rensselaer Polytechnic Institute, Troy, New York 12181

Isothermal P–x data for the ternary system acetone/1,4-dioxane/water at 50 °C are reported, together with data for the constituent binaries. Data reduction by Barker's method provides a correlation for G^E.

Reported here are VLE measurements for the acetone (1)/1,4-dioxane (2)/water (3) system at 50 °C. Experimental values of total vapor pressure are presented for the full composition range of the three constituent binaries and for runs with ternary mixtures formed by addition of each pure species to equimolar, 2:1, and 1:2 mixtures of the other species. The

0021-9568/81/1726-0178$01.25/0