

Table VI.

System	Linear B-H plots	K independent of wave length	ΔH independent of temp.	Total oscillator strength independent of temp.
1:1 CT ^a complex	Yes	Yes	Yes	Yes
1:1 CT complex + contact	Yes	Yes	Yes	No
1:1 CT complex + isomeric 1:1 CT complex	Yes	Yes	No ^c	No
1:1 CT complex + higher order CT complex	Yes ^b	No ^c	No ^c	No
1:1 CT complex, isomeric 1:1 + higher order CT complex	Yes ^b	No ^c	No ^c	No

^a Charge transfer = CT. ^b Theoretical deviation is often too small to be detected. ^c Although the expected deviation may be too small to be detected.

Orgel and Mulliken⁷ point out that two good criteria for the presence of a single complex are the constancy

of ΔH and total oscillator strength with temperature. The criterion of linear B-H plots as proof of the absence of higher order stable charge-transfer complexes has been discussed earlier in this paper. Table VI summarizes the results which would be obtained with various possible systems in regard to the various suggested criteria.

Since the TCNE-naphthalene system yields "nearly" linear B-H plots, the principal absorbing species must be a 1:1 stable charge-transfer complex. In addition to a 1:1 stable charge-transfer complex and a higher order charge-transfer complex, it is possible that isomeric 1:1 complexes as well as contact absorptions are occurring in the TCNE-naphthalene system.

The temperature dependence of ΔH and total oscillator strength can only confirm the presence of more than one equilibrium but can give no information concerning the nature of the additional equilibria. In the case of additional higher order equilibria, the determined values of ΔH and total oscillator strength will be meaningless. Thus, to determine the presence of higher order complexes, the variation of K with wave length must be determined.

Application of High-Temperature Mass Spectrometry to the Determination of the Enthalpy-Composition Function of Nonstoichiometric Binary Compounds¹

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The application of high temperature, Knudsen-cell mass spectrometry to the determination of the enthalpy-composition function is shown for nonstoichiometric compounds that have a range of composition and vaporize by decomposition into a volatile component and a solid solution of the same phase. In principle, the temperature dependence of the partial pressure of the volatile component is measured for a constant composition of the solid and a partial enthalpy value derived. The enthalpy-composition function for the whole homogeneity range is obtained accordingly by measurements for different compositions. The approach is demonstrated for praseodymium monophosphide. The partial molal enthalpy of P_2 decomposition, $\overline{\Delta H}_T[P_2]$, for the reaction $(2/x)PrP_{2-x}(s) = (2/x)PrP_{2-x}(s) + P_2(g)$ was found to increase with decreasing P/Pr atomic ratio from 79.5 to 120.5 kcal. over the composition range measured. The suitability and limitations of the proposed method are discussed.

(1) Part of this work was presented at the Fourth Rare Earth Conference, Phoenix, Ariz., April 22-25, 1964, and at the Mass Spectrometry Conference, Paris, Sept. 14-18, 1964.

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I. Introduction

The experimental findings of partial thermodynamic properties of compounds with high melting points and wide homogeneity ranges are rather sparse. This is in particular true for the partial enthalpies. Direct experimental measurements at temperatures above 1000° have been performed for a limited number of cases where experimental conditions were favorable for the method used. E.m.f. measurements involving galvanic cells have been used up to 1400° but become very dependent upon the availability of a suitable ionic conductor if applied above 1000° and upon the true reversibility of the cell reactions. Therefore, little use of this method has been possible for accurate determination of the temperature coefficient of the e.m.f. and thus the corresponding partial enthalpy. The direct measurement of integral enthalpies for different compositions of solid solutions using calorimetric methods has been applied up to 1400°. However, high temperature calorimetry above 1000° causes many delicate problems and is so far limited to certain alloy systems. Measurement of vapor pres-

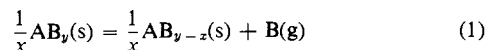
tures at different compositions of a solid solution and temperatures by various methods and derivation of the partial enthalpies are tedious and have not yet been done for many systems, particularly not by measurements at temperatures above 1000°.

The knowledge of the experimentally determined partial thermodynamic properties of nonstoichiometric compounds as a function of composition is necessary for the understanding of their nature, for predicting their behavior in a high temperature environment, and as a basis for improved theories that would have a better predicting power than do existing ones. For this reason, more suitable experimental methods are needed.

The intent of this paper is to demonstrate how partial reaction enthalpies of a binary compound with a substantial range of homogeneity can be determined experimentally by Knudsen-cell mass spectrometry at high temperatures and different compositions of the solid.

II. Method for the Measurement of Partial Enthalpies

Definition of Problem. The suggested method for the experimental determination of the enthalpy-composition function of a binary compound or solid solution AB_y is primarily applicable to those phases that vaporize by decomposition into a single (or predominant) volatile component B and a solid solution AB_{y-x} of the same phase



In order to obtain a second-law determination of the enthalpy of vaporization for this reaction, the temperature coefficient of the partial pressure of B needs to be known. For its measurement the composition x of the solid phase AB_{y-x} must, according to the Gibbs phase law, be fixed.

In a Knudsen cell-mass spectrometer assembly the property measured that corresponds to the partial pressure is the intensity signal I^+ of the singly charged ionic species which is formed by electron bombardment from the neutral vapor species to be measured. It has been shown³ that the product I^+T , where T is the absolute temperature, is proportional to the vapor pressure of the neutral species. As a consequence, if equilibrium may be assumed, the partial enthalpy of reaction 1 for a constant composition x in AB_{y-x} can therefore be determined according to the relation

$$\overline{\Delta H}_T = 4.754T_1T_2 \frac{\log(I_1^+T_1) - \log(I_2^+T_2)}{T_1 - T_2} \quad (2)$$

where I_1^+ is the measured ion intensity of B^+ at the temperature T_1 in °K., and I_2^+ is the ion intensity of B^+ measured at T_2 . The knowledge of the absolute partial pressure of B is not necessary in such a determination.

To test the suitability of the suggested approach, praseodymium monophosphide was chosen. In the course of a study of the vaporization behavior of praseodymium group V compounds⁴ this compound

(3) R. E. Honig, *J. Chem. Phys.*, **22**, 126 (1954).

(4) K. A. Gingerich, "Rare Earth Research. II," K. S. Voores, Ed.,

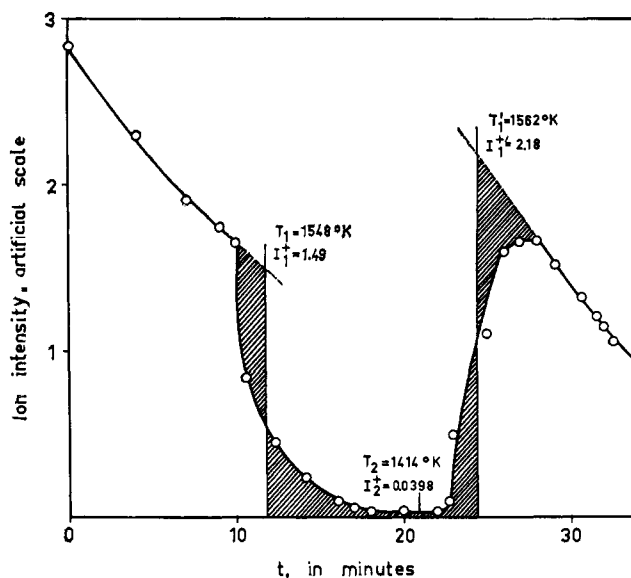
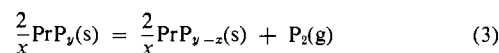


Figure 1. Experimental determination of the temperature dependence of the P_2^+ ion intensity over PrP_{1-x} at constant composition x .

was found to have a marked composition range with a large change in the partial Gibbs free energy of phosphide decomposition as a function of P/Pr atomic ratio in the solid solution. Therefore, an easily detectable change in the corresponding partial enthalpy values of phosphorus decomposition could be expected.

In the temperature range of 1095 to 1548°K. and pressure range of 10^{-9} to 10^{-5} atm., for which data are given below, praseodymium monophosphide, PrP_y , where y is approximately 1, vaporizes predominantly according to



For selected intermediate stages of the investigation, the composition of the solid phase PrP_{1-x} was derived from the starting composition $PrP_{1.00}$ by correlating the total intensity-time integral of the P_2^+ ion with the total change of x in PrP_{1-x} .⁵ In this correlation, proportionality between the corresponding increments of the intensity-time integral for P_2^+ , which were corrected with respect to a chosen reference temperature, and the increments of x in PrP_{1-x} was assumed.⁶

Methodical Procedure. To obtain the temperature dependence of the B^+ ion intensity for a vaporization process of the type expressed by eq. 1, the procedure illustrated in Figure 1 was used. The solid line corresponds to the ion intensity of B^+ measured as a function of time, that is, of increasing x in AB_{y-x} . The experimental data presented correspond to the ion intensity of P_2^+ measured over praseodymium monophosphide.⁷

The ion intensity of B^+ (P_2^+ in the example used) is monitored and its intensity-time relationship determined for a period of time at a comparatively high

Gordon and Breach Science Publishers, New York, N. Y., 1964, pp. 245-255.

(5) M. G. Inghram and J. Drowart, "High Temperature Technology," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 219-240.

(6) Further experimental details are described in the Experimental section below.

(7) See temperature cycle 4 in Table I.

Table I. Experimental Partial Molal Enthalpies of P₂ Decomposition (in kcal.) for PrP_{y-x} as a Function of Composition *x*

	Temp. cycle no.			
	1	2	3	4
Composition <i>x</i> (relative value) ^a	0.041	0.109	0.137	0.145
<i>T</i> ₁ , °K.	1267	1270	1417	1548
<i>I</i> ₁ ^{+b}	16.65	2.82	1.185	1.49
<i>T</i> ₂ , °K.	1095	1155	1271	1414
<i>I</i> ₂ ^{+b}	0.133	0.0845	0.0149	0.0398
<i>T</i> ₁ ['] , °K.	1270	1259	1430	1562
<i>I</i> ₁ ^{+b}	16.63	2.04	1.80	2.18
$\overline{\Delta H}_T$ before cycle	79.8	91.3	109.9	119.9
$\overline{\Delta H}_T$ after cycle	78.6	90.9	111.5	121.6
$\overline{\Delta H}_T$ (weight av.)	79.4	91.2	110.4	120.5

^a As a consequence of the probable error in *x* of the end product these *x* values should be multiplied by a factor smaller than 1. ^b Arbitrary unit.

temperature *T*₁. In this way, the slope of the decreasing B⁺ ion intensity is obtained as a function of time, that is, as a function of *x* in AB_{y-x}. Then the temperature is dropped by 100 to 200° where the ion intensity is small but measurable, and thermal equilibrium at the low temperature is established. After a constant low temperature *T*₂ is reached, as indicated from pyrometer readings, several intensity readings are taken and averaged in order to obtain a reliable low temperature ion intensity value *I*₂⁺ corresponding to the temperature *T*₂. At these low temperatures and ion intensities, no appreciable change in composition *x* in AB_{y-x} takes place. Under the conditions applied during the period in which the praseodymium monophosphide sample was at the low temperature *T*₂ (see Figure 1), the change of *x* in PrP_{y-x} would be ≈0.00001. After having established a reliable ion intensity value *I*₂⁺ at *T*₂, the temperature is raised to *T*₁['], a temperature similar to *T*₁; and, after the attainment of equilibrium, the ion intensity change is again determined as a function of time.

The ion intensity vs. time curves measured at the temperature *T*₁ and *T*₁['], respectively, are then extrapolated to their respective points that correspond to the composition at which the low temperature value *I*₂⁺ was measured. The normalization to a value corresponding to this composition is performed for *I*₁⁺ and *I*₁⁺['] independently, as Figure 1 shows. In this normalization the intercept is chosen such that the areas above and below the measured ion intensity vs. time curve on each side of the low temperature value (at the time of approximately 21 min. in Figure 1) are made equal.⁸ The extrapolation is shorter for the value *I*₁⁺ obtained at the beginning of the temperature cycle than for the value *I*₁⁺['] obtained at the end of the cycle and is therefore more reliable. *T*₁ and *T*₁['] are not necessarily the same, but they are similar in order to check the reliability and the reversibility of the

procedure and the presence of a possible diffusion barrier. In order to obtain partial enthalpy values for different values of *x* in AB_{y-x} the temperature cycle is repeated at several compositions of the solid. Its completion takes longer at lower temperatures owing to the smaller rate in the attainment of temperature equilibrium.

Each of the sets *I*₁⁺*T*₁, *I*₂⁺*T*₂ and *I*₁⁺[']*T*₁['], *I*₂⁺*T*₂ obtained for the same composition *x* in AB_{y-x} is evaluated according to eq. 2 for a mean value of the partial molal enthalpy of B decomposition at *T* = (*T*₁ + *T*₂)/2. The two values obtained for the same composition provide a check on the precision of the measurement and on the influence of a possible composition-dependent diffusion barrier for the vaporization process.

Experimental Results for Praseodymium Monophosphide. Experimental results for the measurement of the partial molal enthalpy of P₂ decomposition are given in Table I for reaction 3. The data presented correspond to a series of measurements that were performed during single thermal degradation of a praseodymium monophosphide sample under conditions for which reaction 3 was found to be the predominant one. In the course of this degradation series four cycles of the type described in Figure 1 were taken.

The experimental results given in Table I show that there is a marked increase in the partial molal enthalpy of P₂ decomposition with increasing *x* in PrP_{1-x}. The two enthalpy values obtained for a constant P/Pr atomic ratio of the solid are in good agreement with one another. From this agreement a precision of better than ±1 kcal./mole of P₂ or approximately 1% can be derived for the partial enthalpy determination. This limit of precision includes the possible error caused by a possible diffusion barrier. It does not include the possible error caused by a possible extremely small temperature-dependent vaporization coefficient or by inaccuracies of the temperature measurement or the presence of a temperature gradient. With respect to the latter two factors, the accuracy of the $\overline{\Delta H}$ values is estimated to be better than 3 kcal./mole.

III. Discussion

The partial enthalpies of vaporization, obtained by the described approach, are based on intensity measurements at the terminal temperatures only. This does not permit a check on the linearity of the log (*I*⁺*T*) vs. 1/*T* plot, that would give an additional indi-

(8) To obtain accurate proportionality between a composition increment Δx and the corresponding increment of the intensity-time integral the latter must be multiplied by $(T_{\text{exptl}}/T_{\text{ref}})^{1/2}$, where *T*_{ref} is the reference temperature for which the calculations are carried out. Because of the continuously changing temperature and the impossibility of correlating an equilibrium temperature to each ion intensity measured during this time period of waiting for attainment of equilibrium, such a correction factor cannot be evaluated accurately. Therefore, it has been neglected, which is identical with choosing the reference temperature and experimental temperature to be equal to the arithmetic mean of *T*₁ and *T*₂. This simplification leads to a small error in the normalized intensity values of *I*₁⁺ and *I*₁⁺['], respectively, that is well within the accuracy of the experimental measurement of the ion intensities.

cation as to whether equilibrium conditions are attained, and whether there exists a temperature dependence of the heat capacity $\overline{\Delta C_p}$ for the reaction under consideration.

In principle, intensity measurements at different temperatures could be made by including steps into the cycle represented in Figure 1. Such steps would best be included at the beginning of a cycle, where the temperature is lowered. Each step would require waiting until temperature equilibrium is established. This would, however, lead to a larger extrapolation for the intensity values at the higher or highest temperatures that are to be adjusted to constant composition and thus to an increased error in these values. Since a second-law enthalpy value depends more on the accuracy of the values measured at the terminal temperatures than on that of values measured in the middle of the temperature range covered, the optimum accuracy in the partial enthalpy in our case is expected from the accurate measurement of the ion intensities at the terminal temperatures. It should be noted that the low temperature ion intensity value is, as a rule, the average of a number of intensity-temperature measurements, whereas one high temperature intensity value each corresponding to the same composition of the solid is obtained before and after the temperature cycle. Checks on the reversibility of the $\log(I+T)$ vs. $1/T$ plot could be made by performing several thermal degradation series similar to the one for which data are presented in Table I. In each of such series measurements could be performed at as nearly the same compositions of the solid solution as possible but at different temperatures T_1 and T_2 . The combined results of different series for the same composition would permit a check of the linearity of the $\log(I+T)$ vs. $1/T$ plot. Similarly, thermal degradation series with temperature cycles such as the one described in Figure 1 should be performed to provide partial enthalpy values for all the compositions needed in order to establish the complete enthalpy-composition function.

The established enthalpy-composition function can be used to obtain intermediate enthalpy values for compositions of the solid for which the temperature coefficient has not been measured experimentally. This value can be used to calculate the temperature dependence of the corresponding partial pressure for any composition of the solid from one pressure value measured for that composition. With a Knudsen cell-mass spectrometer combination it is readily possible to measure a decomposition pressure value of **B** for a reaction such as represented by eq. 1 at a defined composition x within the homogeneity range of the phase AB_{y-x} .

From the known temperature and composition function of the partial pressures of **B** for the phase AB_{y-x} the corresponding partial Gibbs free energies and partial entropies can be calculated as functions of composition and temperature in the usual way. Apparent partial Gibbs free energies of formation per mole of P_2 for reaction 3 have thus been calculated for temperatures between 1000 and 1700°K.⁹

The method shown for the determination of partial

enthalpies should be, in principle, applicable to any incongruent vaporization process of a binary compound for which the equilibrium pressure of the more volatile component is considerably larger than that of the less volatile one or that of any vapor species formed by either of the components of the binary compound with impurities present. Similar conditions would apply for binary alloys or multiple component solid solutions that vaporize incongruently.

In cases where vapor species in addition to the predominant vapor component are present, corrections for these additional vapor species are necessary for the correlation of the intensity-time integral to the composition of the solid. Such corrections would require the knowledge of the ionization cross sections and multiplier efficiencies of these species relative to those of the principal species.

The method also requires the absence of a diffusion barrier and of a vaporization coefficient that varies with temperature. Both of these latter factors tend to become smaller, the higher the temperature of investigation. Additional limiting factors arise from possible interactions between the sample or its products with the cell or liner material, the accuracy of the knowledge of the chemical composition of the sample and the residue, and the possibility of overlooking vapor species originating from the sample.

In spite of such complications, Knudsen-cell mass spectrometry is expected to be a suitable tool for the measurement of the composition function of partial enthalpies of refractory compounds with a range of homogeneity at high temperatures for which the mode of vaporization is completely known. It has, in particular, the potential to be applicable to higher temperatures than any other presently known experimental method.

With improvements in instrumental design, in possibilities of temperature measurement and control of temperature gradients, the accuracy could be expected to be improved sufficiently to make the method attractive for investigation of refractory alloy systems, where partial enthalpy changes with composition are expected to be smaller. In favor of applications to alloy system would be that some of the complicating factors such as complexity of vapor or very low vaporization coefficients are expected to be less pronounced.

IV. Experimental

Praseodymium monophosphide was synthesized from the elements. Praseodymium metal filings from Research Chemicals, Phoenix, Ariz., and semiconductor grade red phosphorus from L. Light and Co., Ltd., Colnbrook, Bucks, England, were used. The phosphorus was claimed to be 99.999% pure, and praseodymium, 99.9%. Chemical analysis of the praseodymium for oxygen and nitrogen showed the presence of 0.13 and 0.03%, respectively. For the preparation of praseodymium monophosphide, praseodymium metal filings were weighed inside an argon-filled glove box into a tungsten boat. The tungsten boat with the praseodymium was then placed together with a weighed amount of red phosphorus into a Vycor tube and sealed under high vacuum. A stoichiometric Pr:P ratio of 1:1.1 was used. The tube with the reactants was heated in a gradient furnace for 12 days with the

(9) K. A. Gingerich in "Advances in Mass Spectrometry," Vol. III, Institute of Petroleum, London, in press.

praseodymium at 900° and the "cool" end of the tube at 400° (to provide a phosphorus pressure of approximately 1 atm.). The praseodymium filings appeared to be completely reacted and the product homogeneous, whereas a small amount of unreacted phosphorus could still be observed. The atomic P/Pr ratio of the product as obtained from the weight gain of praseodymium was 1.00 ± 0.04 after correcting for the phosphorus take-up of the tungsten boat and taking into account an uncertainty in the oxygen content. The uncertainty in the oxygen content comes from the necessity of exposing the sample to air for a short period of time on connection with the later mass spectrometric investigation. The X-ray diffraction analysis indicated a single cubic phase with NaCl-type structure and a lattice parameter of $5.9086 \pm 0.0007 \text{ \AA}$. This compares with a lattice parameter of 5.872 \AA selected as the best value by Iandelli¹⁰ from previous investigations.

For the mass spectrometric experiments, a 60°-sector, 12-in.-radius, single-focusing Nuclide Corp. mass spectrometer was used. The sample was contained in a tungsten liner inside a tungsten effusion cell. Heating was done by radiation from tungsten ribbon filaments suspended around the cell. A calibrated optical pyrometer, focused on a blackbody hole in the bottom of the cell was used for the temperature measurement. Necessary prism and window corrections were applied. The mean free path of the molecules inside the Knudsen cell was not less than 5 mm. The molecular beam was ionized with 55-e.v. electrons. The intensity I^+ of the P_2^+ ion, the principal ionic species, was recorded as a function of temperature and time. At temperatures below 1550°K. praseodymium monophosphide was found to vaporize according to eq. 3. Tetrameric phosphorus was also observed in minor amounts which varied depending on temperatures and pressures. Monatomic phosphorus was identified from its ionization efficiency curve as a fragmentation product.¹¹

(10) A. Iandelli, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, pp. 135-141.

At temperatures above 1500°K., gaseous praseodymium monoxide, apparently originating from the oxygen impurity of the sample, appears in the vapor. At temperatures above 1800°K., additional reactions involving the sublimation of PrP_{y-z} by decomposition into the elements apparently set in, and primary monatomic phosphorus, as identified from the appearance potential and shape of the ionization efficiency curve for P^+ , becomes an important species besides P_2 .

The end product of the thermal degradation at temperatures between 1095 and 1550°K. was analyzed by X-ray powder diffraction and found to be pure praseodymium monophosphide with a lattice parameter of $5.9030 \pm 0.0008 \text{ \AA}$. The P/Pr atomic ratio in this residue, as obtained from the weight loss was 0.85, corresponding to a value of $x = 0.15$ in PrP_{1-x} . In calculating this value, it was assumed that the total weight loss was due to phosphorus. Possible contributions to the weight loss by other unobserved vapor products, such as gases absorbed by the original sample or phosphorus oxides, would result in a smaller value of x . In fact, preliminary results of the investigation of the lattice parameter composition function for praseodymium monophosphide indicate that the change in atomic P/Pr ratio that corresponds to the difference in lattice parameters of the starting material and end product is smaller than 0.1.¹²

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(11) K. A. Gingerich, *J. Phys. Chem.*, **68**, 768 (1964).

(12) K. A. Gingerich and G. R. Eulenberger, unpublished work, 1964.