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WADD TECHNICAL REPORT 60-782
PART VI

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VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

PART VI. STUDIES OF THE VAPORS OF THE SYSTEMS
Au-Cr AND Au-Pd BY MASS SPECTROMETRY

MARCEL ACKERMAN
FRED E. STAFFORD
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UNIVERSITY OF BRUSSELS

NOVEMBER 1961

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AERONAUTICAL SYSTEMS DIVISION

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NOVEMBER 1961

DIRECTORATE OF MATERIALS AND PROCESSES
CONTRACT No. AF 61(052)-225
PROJECT No. 7350

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735001, "Ceramic and Cermet Materials Development." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1960 to March 1961.

WADD Technical Report 60-782, Part I and Part II, have already been published, Part III and Part V are in preparation, with Part IV to follow when it becomes available.

The authors are grateful to Professor Paul Goldfinger for his great help and encouragement. Dr. Jean Drowart aided us with several useful conversations. Part of the equipment has been made available by the Comité Belge de Spectrométrie de Masse (I.R.S.I.A.).

ABSTRACT

The molecules Au-Cr and Au-Pd have been identified. From the data for the reaction $\text{Au}_2 + \text{X} = \text{AuX} + \text{Au}$, and $D_0^\circ(\text{Au}_2) = 51.5$ kcal/mole:

$$D_0^\circ(\text{AuCr}) = 50.4 \pm 3.5 \text{ kcal/mole}$$

$$D_0^\circ(\text{AuPd}) = 33.3 \pm 5 \text{ kcal/mole}$$

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RAMKE

Chief, Ceramics and Graphite Branch
Directorate of Materials and Processes

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INTRODUCTION

Many gaseous molecules containing only "metal" atoms are known and their spectroscopic and/or thermodynamic properties measured (1, 2, 3).

-
- (1) G. Herzberg, Spectra of Diatomic Molecules, (Van Nostrand, New-York, 1945).
 - (2) M.G. Inghram and J. Drowart, in High Temperature Technology, Proceedings of an International Symposium; (Mc Graw Hill, New-York, 1960).
 - (3) Ackerman, Stafford and Drowart, J. Chem. Phys. 33, 1781 (1960) and references cited therein.
-

However, among all these molecules, there are none containing transition element atoms. This has instigated an investigation⁽⁴⁾ on the stability of the homonuclear diatomic transition metal molecules.

-
- (4) Verhaegen, Stafford, Goldfinger and Ackerman, XVIII th International Congress of Pure and Applied Chemistry, Montreal, August, 1961;
-

This study indicates special interest in molecules with Cr and Pd because of the experimental conditions on the one hand, and their unusual electronic configurations (d^5s^1 and d^{10}) on the other.

The present work reports D_0° (AuCr), D_0° (AuPd), and measured upper limits of D_0° of Cr_2 and Pd_2 .

Manuscript Released by the Authors August 1961 for publication as an ASD Technical Report.

EXPERIMENTAL.

The general experimental set up and procedure already have been described^(3,5). Samples were prepared in situ by melting together weighed quantities of the 99.9% pure metals

(5) Ackerman, Drowart, Stafford and Verhaegen, J. Chem. Phys. 0000 (preceding article).

in such proportions as to give approximately equal partial vapor pressures. The samples were contained in either alumina or spinal crucibles⁽⁶⁾ placed in a molybdenum Knudsen effusion cell; effusion orifice to sample surface area was about 1 : 50,

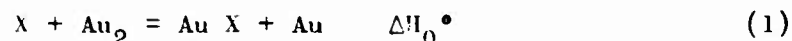
(6) Degussit Al 23 or Sp 23, Degussa, Hanau.

EXPERIMENTAL DATA.

Ions corresponding to Au^+ , Cr^+ , Pd^+ , Au^{++} , Cr^{++} , AuCr^+ , and AuPd^+ were observed and identified by means of isotopic ratios. When ionized by nominal 70 eV electrons, $I(\text{Cr}^{++})/I(\text{Cr}^+)$ was observed to be 0.06. Using the ratio of secondary multiplier efficiencies $\gamma(\text{Cr}^+)/\gamma(\text{Cr}^{++}) \cong 0.5$ ⁽⁷⁾ we have $\sigma(\text{Cr} \rightarrow \text{Cr}^{++})/\sigma(\text{Cr} \rightarrow \text{Cr}^+) \approx 0.03$

(7) R.E. Fox, J. Chem. Phys. , 33, 200 (1960)

Table I presents for the systems Au-Cr and Au-Pd the measured ratios of ion intensities, corrected for isotope ratios and for ionization and secondary multiplier efficiencies. The first column gives the number of the experiment and the index of point (the data are arranged in order of increasing temperature); the second column the absolute temperature; the third the equilibrium constant for the reaction.



where X is Cr or Pd; the fourth column, $\eta_0^\circ(AuX) = \eta_0^\circ(Au_2) - \Delta H_0^\circ$

Fig 1 shows $\log \left[I(Cr^+)I(Au^+)T/I(AuCr^+) \right]$ as a function of $10^4/T$, where I is the ion current in arbitrary units and T the absolute temperature.

Table II gives data for calculating upper limits for $\eta_0^\circ(Cr_2)$ and $\eta_0^\circ(Pd_2)$. In this case, the third column is the equilibrium constant for the reaction :



The fourth column gives $\eta_0^\circ(X_2) = \Delta H_0^\circ(a) + \Delta H_0^\circ(vap.X)$

TREATMENT OF EXPERIMENTAL DATA

The enthalpy change at 0°K, ΔH_0° for reaction (1) was calculated using the relation

$$\Delta H_0^\circ = -RT \ln \left[\frac{I(\text{AuX}^+) I(\text{Au}^+) \sigma_Y(\text{Au}_2) \sigma_Y(\text{X})}{I(\text{Au}_2^+) I(\text{X}^+) \sigma_Y(\text{AuX}) \sigma_Y(\text{Au})} \right] - T \Delta \left[(F^\circ - H_0^\circ)/T \right] \quad (2)$$

where the symbols have the same meaning as in the preceding article⁽⁵⁾. For reaction (1a) the appropriate equilibrium constant and $\Delta(\text{fef})$ were substituted in the right hand side of Eq.(2).

Values for the relative ionization cross sections were taken from Otvos and Stevenson⁽³⁾ except that of Au which was determined previously⁽³⁾. As a check on the calculations for Cr,

(8) J.W. Otvos and D.P. Stevenson, J. Am. Chem. Soc., 78, 546 (1956).

the quotient $\sigma_Y(\text{Cr})/\sigma_Y(\text{Au})$ was calculated from data for a quantitative vaporization of an alloy containing 249 mg Au and 61.4 mg Cr. We use the relation

$$\sigma_Y(\text{X}) S' = (S/G)(M/2\pi R)^{1/2} \sum_t I(\text{X}) T^{1/2} \Delta t \quad (3)$$

where S' is characteristic of the instrument; s the effective area of the effusion orifice; G the number of grams of material evaporated; R the gas constant; T the absolute temperature and Δt the time increment.

In the case of a simultaneous vaporization, S' and s cancel. Using the previously determined⁽³⁾ values of the secondary electron multiplier efficiency γ , the calculated ratio $\sigma(\text{Cr})/\sigma(\text{Au})$ is a factor of 1.5 ± 0.4 lower than the value inferred from Otvos and Stevenson.

As the difference is just on the limit of being significant, the relative cross section given by the latter authors was used.

For the diatomic molecules it was assumed that the cross section is the sum of cross sections for the atoms⁽⁸⁾.

Free energy functions for the gaseous atoms were taken from the compilation of Stull and Sinke⁽⁹⁾. Those of the diatomic molecules were calculated⁽¹⁰⁾ using the estimated interatomic,

(9) G.C. Stull and D.R. Sinke "Thermodynamic Properties of the Elements." (American Chemical Society, Washington D.C. 1956).

(10) K.S. Pitzer, "Quantum Chemistry" (Prentice-Hall Inc.) Englewood Cliffs, New Jersey, 1953.

distances, vibration frequencies and electronic multiplicities given in Table III. Although there are numerous empirical formulae⁽¹¹⁾ relating internuclear distance and vibration frequency,

(11) See survey by E. Clementi, Ann. Chim. 50, 548 (1960)

the necessary parameters are not available for the type of molecules studied here. The interatomic distances used are those given by Pauling⁽¹²⁾. The vibration frequencies for the asymmetric molecules were calculated using

- (12) L. Pauling, J. Am. Chem. Soc., 69, 542 (1947); "The Nature of the Chemical Bond", Cornell University Press, New-York (1960)

Gordy's⁽¹³⁾ correlation between electronegativity, inter-atomic distance and force constant.

- (13) W. Gordy, J. Chem. Phys., 14, 305 (1946)
-

For Cr₂ and Pd₂ the frequencies were chosen arbitrarily in keeping with the electronic configuration of the atoms : d⁵s¹ for Cr and d¹⁰ for Pd⁽⁴⁾.

THE DISSOCIATION ENERGIES

This is believed to be the first observation of the molecules AuCr and AuPd. The measured dissociation energies are given in Table I, the final results being 50.4 ± 3.5 and 33.3 ± 5 kcal/mole for AuCr and AuPd respectively. These are based on the value $D_0^\circ(\text{Au}_2) = 51.5 \pm 2.2$ kcal/mole. The absolute uncertainties are estimated using the following figures.

A 20 % error in internuclear distance or 30 % error in vibration frequency causes 1.2 kcal/mole error in D_0° calculated from measurements made at 1.700° K.

A 70 % uncertainty is admitted in the ionization section and secondary electron multiplier efficiency rates. An uncertainty of 40° possibly exists between the temperature measured at the blackbody hole and that which determines the equilibrium in the cell. Uncertainty in D_0° arising from uncertainty in the multiplicity of the ground and low lying electronic levels may be quite significant in molecules formed from atoms with many unpaired electrons. The calculated dissociation energies may be corrected easily when the

necessary data become available, noting that the multiplicity m of the ground electronic state enters into η_0° as $RT \ln m$. If the uncertainty in m is a factor of two as it may well be for AuCr, the resulting uncertainty in η_0° measured at 1700°K is 2.3 kcal/mole.

From the slope obtained from Fig. 1, and estimated heat capacities, the "second law" $\eta_0^\circ(\text{AuCr})$ is calculated to be 52.6 kcal/mole. The result is in good agreement with the "third law" value from Eq.(1). In view of the well known uncertainties in the "second law" measurements made at high temperatures, it is not considered advisable in this case to use comparison between the second and third law to give information on the electronic entropy of AuCr.

The measured upper limits of the partial pressures of $\text{Cr}_2(\text{g})$ and $\text{Pd}_2(\text{g})$ presented in Table II give upper limits of η_0° of 40 and 33 kcal/mole respectively. These values are calculated using $\Delta H^\circ(\text{var}, \text{Cr}) = 95.5^{(9,14)}$ and $\Delta H_0^\circ(\text{vap}, \text{Pd}) = 84.5^{(15,16)}$ kcal/mole.

(14) O.Kubaschewski and G. Heymer, *Acta Meta.*, 8 416 (1960)

(15) Selected Values for the Thermodynamic Properties of Metals and Alloys, Minerals Research Laboratory, University of California, Berkeley, 1960.

(16) J.F. Haefling and A.H. Daane, *Trans. Met. Soc. AIME*, 212 115 (1955).

DISCUSSION

In both AuCr and AuPd, the forces which cause bonding are considerable and give rise to appreciable bond energies. The 18 kcal/mole difference in the bonding energy between AuCr and AuPd may be correlated with the ground electronic configuration of Cr and Pd atoms. Chromium ($d^5 s^1, ^7S$) has an unpaired s electron which may combine with the s electron of Au ($d^{10} s^1, ^2S$), whereas Pd ($d^{10}, ^1S$) has a quasi-rare gas configuration and bonding is due presumably to interactions with excited states. In keeping with the availability of low lying excited levels of Pd, this interaction is quite effective compared to that in molecules containing Au and other closed sub-shell atom such as Ca or Mg. The dissociation energies of Au₂, Ca₂, and AuMg are appreciably lower, of the order of 20 kcal/mole⁽¹⁷⁾

(17) J. Schiltz, Compt. Rend. 252, 1750 (1961)

J. Ruamps, Ann. Phys. 134, 1111 (1959)

The greater stability of AuCr relative to AuPd is expected also on the basis of a relation of Pauling⁽¹¹⁾ which states that single bond energy of XY is the arithmetic mean of the single covalent bond energies of X_2 and Y_2 plus an "ionic" contribution proportional to $(\chi(X) - \chi(Y))^2$ where the χ are electronegativities. On the basis of estimated electronegativity values, AuCr is expected to have much greater ionic stabilization than AuPd. However use of Pauling's relation to estimate the D_0° of the symmetric molecules Cr₂ and Pd₂ is not considered to be reliable.

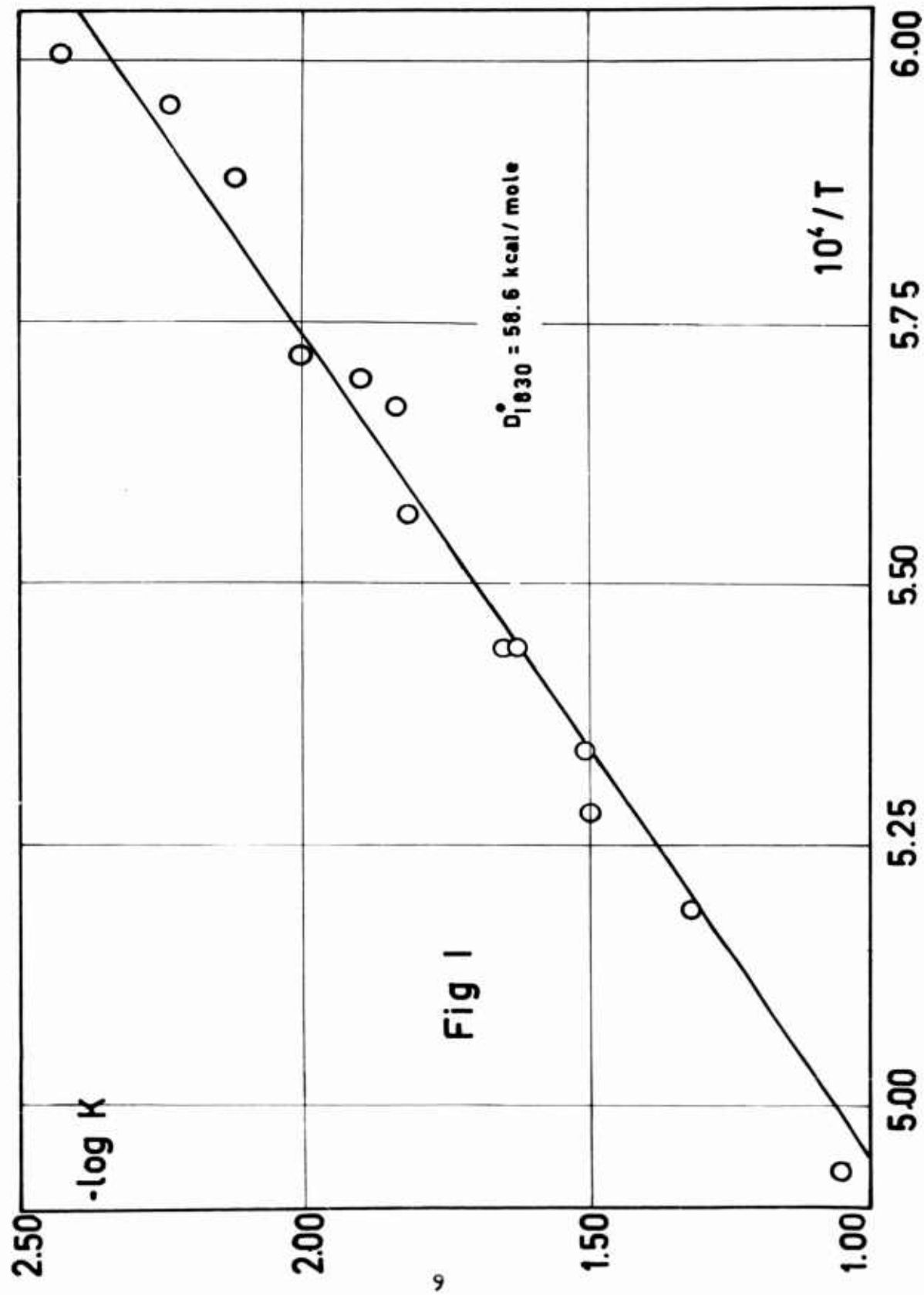


TABLE 1. Measured Pressure Ratios and Calculated Dissociation Energies of AuCr and AuPd.

Exp.	T°K	$\log \frac{p(\text{AuX})p(\text{Au})}{p(\text{Au}_2)p(\text{X})}$	$D_0^\circ (\text{AuX})$ kcal/mole
AuCr			
3.8	1697	0.426	50.7
3.12	1748	0.450	50.8
3.7	1780	0.412	50.5
3.13	1837	0.514	51.3
3.6	1838	0.403	50.4
3.9	1873	0.447	50.8
3.14	1893	0.544	51.6
3.10	1928	0.465	50.9
		mean	50.9
15.7	1637	0.658	50.5
15.1	1670	0.101	48.2
15.6	1708	0.395	50.4
15.2	1738	0.214	49.0
15.8	1739	0.585	51.9
15.9	1810	0.541	51.6
15.3	1814	0.142	48.3
15.5	1831	0.240	49.1
15.10	1893	0.288	49.4
		mean	49.8
AuPd		mean of all points	50.4
1.1	2013		
14.1	2045	1.08	33.2
		1.04	33.4
		mean	33.3

$D_0^\circ (\text{AuX}) = D_0^\circ (\text{Au}_2) - \Delta H_0^\circ$ where ΔH_0° is for the reaction

$\text{Au}_2(\text{g}) + \text{X}(\text{g}) = \text{AuX}(\text{g}) + \text{Au}(\text{g})$ and where $D_0^\circ (\text{Au}_2) = 51.5$ kcal/mole

TABLE II. Limits of Pressure Ratios and calculated
Dissociation Energies of Cr_2 and Pd_2

System	T°K	$\log P_x/P_{x_2}$	$D_0^0(X_2)^*$
Cr	1909	4.93	40
Pd	1920	3.55	32

$$* D_0^0(X_2) = \Delta H_0^0(\text{vap.}X) - \Delta H_0^0$$

where ΔH_0^0 is for reaction $X_2(g) \rightarrow X(g) + X(s)$ and

$\Delta H_0^0(\text{vap.}Cr) = 95.5 \text{ kcal/mole}$ and $\Delta H_0^0(\text{vap.}Pd) = 84.5 \text{ kcal/mole}$.

TABLE III. Parameters Used for Calculation of Free Energy
Functions of Diatomic Molecules.

Molecule	Vibration frequency cm^{-1}	Internuclear distance $\text{\AA}$	Multipli- city M	Relative cross section x Mult. Eff.
Au	191	2.68	1	22.6
AuCr	250	2.44	6	24.9
AuPd	200	2.60	2	21.1
Cr ₂	250	2.34	1	44.4
Pd ₂	70	2.56	1	19.5