VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

Part I. Mass Spectrometric Determination of the Dissociation Energies of the Molecules AgAu, AgCu, and AuCu.

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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 Nonmetallic Materials," Task No. 73500, "Ceramic and Cermet Materials Development". The work was administered under the direction of Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1959 through March 1960.

The authors wish to thank Professor Paul Goldfinger of the University of Brussels for his constant encouragement and counsel. Acknowledgment is due the Comite Belge de Spectrometric de Masse (I.R.S.I.A.) for making available part of the equipment used in this project.

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The vapors issuing from mullite and Graphite Knudsen cells containing pure metals and alloys of the triad Cu-Ag-Au have been analyzed mass spectrometrically. From the experimental ratios of diatomic to monoatomic species and the vapor pressures of the elements, the following dissociation energies are obtained:

$$D_o^o (Cu_2) = 43.2 \pm 2.2 \text{ kcal} \qquad D_o^o (AgAu) = 47.6 \pm 2.2$$

$$D_o^o (Ag_2) = 35.7 \pm 2.2 \text{ kcal} \qquad D_o^o (AgCu) = 40.7 \pm 2.2$$

$$D_o^o (Au_2) = 51.9 \pm 2.2 \text{ kcal} \qquad D_o^o (AuCu) = 54.3 \pm 2.2$$

These are based on $H_{298}^{vap} = 81.1$, 68.4 and 87.5 cal/mole for Cu, Ag and Au where D_o^o of AgAu depends on the value for Cu, and D_o^o of AgAu and AuCu on Au. The uncertainties quoted do not include the uncertainty in ΔH^{vap}.

These results are interpreted in terms of chemical bonding theories. The relation between bonding in the gas and in the pure condensed phases is again observed. Furthermore, a previously unobserved qualitative relation between the dissociation energy of the asymmetrical molecule and the heat of formation of the corresponding alloys is indicated.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. G. RAMKE
Chief, Ceramics and Graphite Branch
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Introduction.

The symmetric molecules Cu_2, Ag_2 and Au_2 have been identified and studied by optical spectroscopy in emission and in absorption by Ruamps (1), and by Kleman, Lindkvist and Selin (2-3). Vibration

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(1) J. Ruamps, Compt.rend. <u>237</u>, 1489 (1954).

(2) B. Kleman and S. Lindkvist, Arkiv Fys, <u>8</u> 333 (1954); <u>9</u>, 385 (1955).

(3) Kleman, Lindkvist and Selin, Ark. Fys. <u>8</u> 505 (1954).

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frequencies and dissociation energies from linear Birge-Sponer extrapolations were obtained. Drowart and Honig (4) and Schissel (5)

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(4) J. Drowart and R.E. Honig, J. Chem. Phys., <u>25</u>, 581 (1956); J Phys Chem <u>61</u> 980 (1957)

(5) P. Schissel, J. Chem. Phys., <u>26</u>, 1276 (1957).

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used mass spectrometric technique to study the species vaporizing from the pure metals. They indentified the symmetric diatomic molecules and determined the heats of dissociation. Martynkevitch (6), Rosenstock (7), and Searcy, Freeman and Michel (8) have observed

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(6) G.M.Martynkevitch, Vestnik, Loskov Univ. Ser.Mat,Mekn, Astron., Fiz., Khim., 13,151 (1958);C.A.,53, 5796h (1959).
(7) H.M.Rosenstock, in Electromagnetically Enriched Isotopes and Mass Spectrometry, ed. N.L.Smith, Butterworth, London (1956) p. 155. (S) Searcy. Freeman and Michel, J.Am. Chem. Soc. 76 4050 (1954).

triatomic ions of copper or of silver.

The asymmetric molecules. AgAu, AgCu, and AuCu were observed spectroscopically by Ruamps (9-10). The species AuCu were observed by Schissel (5), while all three asymmetric molecules were observed by Ackerman. (11).

(9) J.Ruamps Compt.rend. 239 1200 (1954)
(10) J. Ruamps Colloqium Spectroscopium International VI (Amsterdam, 1956), Pergamon, London.
(11) M. Ackerman, Ind. Chim. Belg., 25, 0000 (1960)

The present paper reports a mass spectrometric determination of the dissociation energies of the symmetric and asymmetric diatomic molecules in equilibrium with binary Cu-Ag-Au alloys. Particular emphasis has been placed on obtaining values of dissociation energies that are accurate relative to one another.

Experimental.
Binary alloys were prepared by mixing together weighed quantities of the 99.9% pure metals and melting them in the mass spectrometer. The initial composition was generally about 90 at-% of the less volatile constituent.In all cases,

the more volatile constituent was found to distill off quantitatively leaving behind the other constituent essentially pure.

The alloys were vaporized from electron-bombardment heated (12) Knudsen cells with 1-mm diameter orifices and orifice to sample surface ratio of about 1/100. In the early experiments,

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(12) W.A. Chupka and M.G. Inghram, J.Phys. Chem., 59, 100 (1955).

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graphite Knudsen cells were used; however, particularly in the case of gold, during the course of an experiment the monomer intensity was observed to decrease appreciably, and the dimer/monomer ratio, taken at constant temperature, similarly decreased by as much as a factor of ten. Examination of a ball of gold that remained after such an experiment showed that it was covered by a heavy layer of graphite. As a result, experiments were made using a molybdenum outer crucible and an impermeable mullite $(3Al_2O_3.2SiO_2)$ inner crucible, which proved to be satisfactory.

A Leeds and Northrup disappearing filament optical pyrometer was used to measure the brightness temperature of a hole drilled in the bottom of the molybdenum crucible. Calibrations for emissivity were obtained in situ and are given under "Analysis of Data".

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The crucible and source arrangement are significantly different from those used previously in this laboratory and are shown in Figure 1. The pyrometer window A is protected from deposits by the magnetically operated shutter B. The geometry used is such that the pyrometer objective is completely filled by light from the black-body hole in the crucible D. The molecular beam limiting aperture is a one millimeter orifice at J. The density distribution of the deposit on a window on the far side of the source K is the same as that calculated for a one millimeter crucible orifice and the collimation at J. None of the molecular beam strikes any part of the source. A movable beam defining slit H, whose position is fixed by a micrometer screw, permits us to distinguish between ions formed from species in the molecular beam, from species possibly reevaporating from the radiation screens and from the residual gases in the source (13).

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(13) M.G. Inghram and J. Drowart, "Mass Spectrometry Applied to High Temperature Chemistry," Proceedings of a conference, Asilomar, Calif. 1959.

Pumping speed in the region of the source and the furnace is about 10 liters/sec.

The ion source is the same as used previously (4,14)

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(14) J. Drowart and P. Goldfinger, J. Chim.Phys., 55
72 (1958).

Ions were formed by a 3 to 30 μA beam of 5 to 70 volt
electrons and accelerated to 2000 eV.

The ions formed were mass analysed by a 20-cm.
radius of curvature, 60° sector, single focusing mass
spectrometer with a resolving power of 1/700 (Rayleigh
criterion). The ion current leaving the exit slit was
further accelerated to 4500 eV, amplified by a nine
stage Ag-Mg secondary electron multiplier, and then
measured by a vibrating reed amplifier and pen rec-
order. Species were identified (13) by mass, isotope
ratio, appearance potential and dependance of in-
tensity on the position of the movable beam defining
slit H.

Experimental Data.

In addition to the atoms, only the six symmetric
and asymmetric diatomic molecules were observed. Table
I presents the observed ratios of diatomic to mono-
atomic molecules corrected for ionization cross section
and multiplier efficiency. The first column of the
table indicates the number of the experiment ; the
second, the absolute temperature ; the third, the ratio
of molecule pressure to that of the more volatile atomic

species ; and the last, the value of the dissociation energy calculated by Eq. (1). Values indicated by an asterisk are averages of 3 to 5 consecutive readings taken at a given temperature.

Treatment of Data.

The dissociation energies D_o^o were calculated using the relation

$$D_o^o = - RT \ln \frac{I(Y)\, \sigma\gamma\,(XY)}{I(XY)\,\sigma\gamma\,(Y)}\, p(X) - T\left[\frac{F^O - H_o^o}{T}\right] \tag{1}$$

where $I(Y)$ is the ion current due to species Y ; σ the ionization cross section ; γ the relative efficiency of the secondary electron multiplier ; $p(X)$ the vapor pressure of the less volatile species X ; and $(F^O - H_o^O)/T$ the free energy function.

Values for the relative ionization cross sections of Cu and Ag were taken from Otvos and Stevenson (15). The value for Au was

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

calculated from data for a quantitative vaporization of a Cu-Au alloy in the mass spectrometer with a classical collector. Equation (2) presents the relation between ion intensity and ionization cross sections

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$$\sigma(X) \, \gamma(X) S' = (s/G) \, (M/2\pi R)^{1/2} \sum_t I(X) \, T^{1/2} \Delta t \tag{2}$$

where γ is unity for a classical collector, S' is characteristic of the instrument, s is the area of the effusion orifice, G the number of grams evaporated, M the molecular weight, R the gas constant, T the absolute temperature, and t the time. When comparison is made between two substances evaporated simultaneously, S' and s cancel. The value obtained is

$\sigma(Au) / \sigma(Cu) = 35/18.4$.

For the diatomic species we assume $(XY) = (X) + (Y)$.

The multiplier efficiency, as a function of mass only, was determined experimentally from data for a mixture of rare gases and from quantitative vaporizations of alloys. Molecular effects were calculated as suggested by Stanton, Chupka and Inghram. (16). The values used are shown in Table II.

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(16) Stanton, Chupka and Inghram, Rev. Sci. Inst., 27, 109 (1956).

The temperature scale of the pyrometer was verified by observing the melting point of Cu, Ag, and Au. The experimental arrangement consisted of a block of graphite

under a hydrogen atmosphere in an electrically heated quartz tube furnace. One hole in the graphite block served as a "black body" while an adjacent served as sample holder.

(17) D.R. Stull and G.C. Sinke, Thermodynamic Properties of the Elements, Advances in Chemistry, Series 18, Am.Chem.Soc., Washington, D.C., 1958.

In addition, an in situ calibration described by Johnson, Hudson, Caldwell, Spedding, and Savage (18) using the molybdenum

(18) Johnson, Hudson, Caldwell, Spedding, and Savage, J.Chem.Phys., 25, 917 (1956).

cell in the mass spectrometer was performed. This involved measuring the crucible brightness temperature and ionic intensity of the species X^+ at some temperature just above the point of fusion. The heating power was reduced, the cooling curve recorded, and the brightness temperature measured at the lower temperature. Interpolation of the intensities between the higher and lower temperatures measured was achieved using a plot of log I^+T vs 1/T. The observed point of fusion of Au was 40° low. This was attributed to the low emissivity of the molybdenum. Corrections were made

assuming an emissivity of 0.7 (19)

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(19) W.E. Forsythe, "Temperature, Its measurement and control," Reinhold, New York (1941) p. 1183.

The heats of sublimation ΔH_{298}^{vap} of Cu, Ag, and Au were taken as 81.1, 68, 4, and 87.5 kcal. Vapor pressures for Cu and Ag were taken from Stull and Sinke (17). For gold, there is a disagreement between the value given by Stull and Sinke, which is bases on Hall's work (20 f), and the recent

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(20) (a)O.Ruff and G.Bergdahl, Z.anorg.Chem <u>106</u>, 76, (1919); (b), O.Ruff and H. Konschak, Z. Electrochem. <u>32</u>, 515 (1926); (c), P. Harteck, Z. physik Chem. <u>134</u>, 1 (1928); (d) A.Farkas Z. physik Chem B5 467 (1929); (e), E.Bauer and R. Brunner Helv.chim.Acta <u>17</u>, 958 (1934); (f), L.D. Hall, J.Am.Chem.Soc. <u>73</u>, 757 (1951); (g), Nesmeianov, Smakhtin and Lebedev, Doklady Akad.Nauk SSR, <u>112</u>, 700 (1957); (h), R.K. Edwards, private communication; (i), E.G. Rauh, unpublished data.

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determinations of Nesmeianov, Smakhtin, and Lebedev (20 g), Edwards (20 h), and Rauh (20 i). Table III indicates the various values calculated for H_{298}^{vap} for gold, based on the free energy functions of Stull and Sinke (17).

The values of Harteck, and of Bauer and Brunner have been interpreted by Hall as giving upper and

lower limits, Harteck being high because of contamination of his surface (cf Fraser (21)) and Bauer

(21) R.G.J. Fraser, Molecular Rays, Cambridge (1931).

and Brunner low because of inadequate emissivity corrections. We have chosen to use the average of the three most recent determinations, 87.5 kcal.

We have attempted also to measure directly the differences in heats of vaporization of Cu, Ag, and Au. The relation between the ionic intensities due to Ag or Cu and Au and the respective pressure is

$$P(Au)/p(AG) = I(Au) \, \sigma \, \gamma \, (Ag) \, a(Ag) \, I(Ag) \, \sigma \, \gamma \, (Au) \, a(Au) \tag{3}$$

where p are the pressures and a the activities (22).

(22) (a) Selected values for the thermodynamic properties of metals and alloys, Minerals Research Laboratory, University of California, Berkeley ; (b) R.K.Edwards and James H. Downing J.Chem.Phys., *60*, 108 (1956).

Unfortunately, the uncertainty in the activities of the more volatile component Cu or Ag, which activity ranged between 0.0 and 0.1 gives rise to estimated uncertainties in ΔH^{vap} (Au) of 1.5 to 2 kcal. The value obtained by this method is 87 kcal. Similarly,

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one quantitative vaporization experiment, using Eq.

(2) to determine S' , gives 87.3 kcal.

Free energy functions for the monatomic species were taken from Stull and Sinke and were calculated (23) for diatomic species. The vibration frequencies

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(23) K.S.Pitzer, Quantum Chemistry, Prentice-Hall, **Inc.,** New York (1953)

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were taken from the literature (1-3, 9, 10) and the interatomic distances estimated from the crystal radii (24). The vibration frequencies used for Cu_2, Ag_2, AgAu, AgCu, and AuCu are 266.1, 192, 191, 210, 250

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(24) L. Pauling, J.Am.Chem.Soc., 69, 342 (1947).

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and 250 cm^{-1} respectively, while the interatomic distances used are 2.34, 2.68, 2.68, 2.68, 2.51, 2.11, and 2.51 A. Values of r based on the gaseous hydrides or on Ruamps value for Au_2 are systematically smaller but their use would not increase the D_o^o by more than 0.5 kcal. Electronic states were assumed to be $^1\Sigma$

The Dissociation Energies.

The values of the dissociation energies obtained by Drowart and Honig (4), by Schissel (5), and by ourselves are shown in Table IV. All these values have been recalculated using the elemental heats of vaporization and the free energy functions as stated above. In calculating Schissel's data, we have assumed that his ionization cross section-multiplier correction, $\sigma\gamma(X_2)/\sigma\gamma(X)$, is equal to 1.7.

The results from this work and from the linear Birge-Sponer extrapolation are considered to be in good accord.

The agreement between our work and Schissel's is good when we interpret his results under the same assumption for the ionization cross sections used in interpreting D-H's and our own. This is: $\sigma(XY) = \sigma(X) + \sigma(Y)$. The ratio of $\sigma\gamma(X_2)/\sigma\gamma(X)$ used in calculating the D_o^o shown in Table IV is taken to be 1.7, assuming his correction for multiplier efficiency to be 0.85. Actally, one would expect the ratio of γ's for Cu_2/Cu to be smaller than 0.85, tending to bring our results into closer agreement. (Cf, Schissel's paper (5); or Inghram et al. (25) for curves of γ as a function of mass).

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(25) M.G. Inghram and R.J. Hayden, a Handbook on mass spectrometry, NatlRsch. Council Publication N⁰. 311; Inghram, Hayden and Hess in N.B.S. Circ. 522 Washington (1953) p. 257.

Thus we believe the difference between this work and Schissel's is within the limits of experimental error. It should be noted that Schissel worked with 20-volt ionizing electrons, and we with 70. Schissel observed that increasing his ionizing voltage causes the computed value of D_0^0 to decrease, which would tend to bring our two sets of data into closer agreements.

Drowart and Honig's results are systematically 2 kcal higher than ours. In order to determine if this might be a result of the crucible-source arrangement, we performed an experiment with Cu using an arrangement similar to D-H's actual experimental arrangement: a resistance heated, open alumina crucible which was so mounted that all molecules leaving in a solid angle entered the ionization chamber (but, unlike D-H, we used the secondary electron multiplier). The D_0^0 calculated from these open cell measurements is 1.5 kcal higher than that from our Knudsen cell measurements, which is just on the limit

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of experimental error. We believe the present tech-
nique, with the Knudsen cell removed from the source
and with the well collimated molecular beam gives the
more reliable results.

D_T^O calculated from plots of $\ln P(X_2)/P(X)$ vs
$1/T$, even though not dependent on intrumental sensi-
tivities or free energy functions, are, as is well
known much less reliable than those from the third
law. The D_T^O calculated from our own and from the others'
data tend to be   10kcal higher than the third law
D_O^O' s, which is within the limit of error.

The probable error in the absolute value of our
results calculated by the third law is estimated as fol-
lows: the scatter of the various experimental points
for each molecule is about 0.5 kcal (this is $\sim$0.8kcal
for AgCu due to the smaller dimer-monomer ratio).
The error due to an assumed uncertainty of 70% in the
cross sections and multiplier efficiencies gives an
uncertainty of 2 kcal at 1700° K ; a systematic tem-
perature error of 40° would give rise to 0.5 kcal for
Au at 1700° A. No allowance is made for uncertainties
in the free energy function due to interatomic distances,
which may be systematically too large. Exclusive of
uncertainties in the heats of vaporization, this gives
rise to a most probable error of 2.2 kcal.

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A quantity that is of interest is the difference between the experimental $D_O^O(XY)$ and the arithmetic mean of the energies for the symmetric molecules. Since errors made in assuming ionization cross sections and in measuring temperatures would largely tend to cancel in taking differences, we estimate the error in each D_O^O for this purpose 0.5 kcal ; cross sections and multiplier efficiencies 1 kcal : temperature 0.2 kcal, giving a most probable error of 1.1 kcal. The most probable error in the difference is thus 1.4 kcal.

Errors in the heats of vaporization of the atoms for, say, AgAu causes an error in the difference equal to $\triangle$ H(Ag) $+$ 1/2 $\triangle$ H(Au). By "difference", the most probable is ± 1.7 kcal.

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Discussion of results.

Brewer and Searcy (26) have remarked that the

(26) L. Brewer and A.W. Searcy, "High Temperature Chemistry"
Ann.Rev.Phys.Chem., 7 268 (1956).

dissociation energies for the six molecules of the copper
triad should provide extremely interesting tests of bond
theories. The first column of Table V shows the diss-
ociation energies of the asymmetric molecules XY. The
second column shows the arithmetic mean of $D_C^0(X_2)$, and
the third column the difference between the first two
columns. Although there are significant differences,
these differences are not larger than 15 %. In parti-
cular, the two molecules containing Au are distinctly
more stable than predicted by the mean of the symmetric
molecules.

Such behaviour may be interpreted in terms of a
difference of electronegativity (28) for the three atoms.

(28) L. Pauling, Nature of the Chemical Bond, Cornell,
Ithaca, N.Y. (1941).

Electronegativity differences between Cu-Ag, Ag-Au
and Au - Cu are calculated to be 0.24, 0.41, and 0.55,

in good agreement with earlier results of Haissinsky (29).

(29) M. Haissinsky, J.Phys. Rad., 7, 7 (1946).

This behaviour may be attributed to the availability of d orbitals for bonding. Silver, which has the smallest energy of dissociation, also has the relatively most stable d shell indicated by the fact that the atom with next lower atomic number, Pd, has a $d^{10}s^0$ configuration while those preceding Cu and Au (Ni and Pt) have d^8s^2 and d^9s^1 configurations. The silver atom has relatively few low lying d^9 excited levels compared to Cu and Au, and silver compounds normally exhibit only the +1 valence. Similarly, as discussed below, there seems to be a distinct relation between bonding in the gas and in the condensed phases indicating that conclusions made about bond character in the condensed phase apply to the diatomic molecules.

It has been remarked by Pauling that the ratio $\Delta H^{vap}/D_c^o$ is approximately 2 for the group 1A elements (30).

(30) L. Pauling, J.Chem.Phys., 46, 277 (1949).

Similarly, we may use dissociation energies given by

Herzberg (31), Chupka, Berkowitz, Giese and Inghram

(32) and

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(31) G. Herzberg, Molecular Spectra and Moleculer

Structure I : Diatomic Molecules. Van Nostrand,

New York 1951.

(32) Chupka, Berkowitz, Giese and Inghram, J.Phys.Chem.,

62, 611 (1958).

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by ourselves to calculate the same ratio for the groups

IIIB, III and IB. This ratio systematically is equal to

2, which leads one to believe that bonding in the gas

and in the condensed phases is similar for these metals.

Thus the stability of the row VI transition metals,

apparently due to the d electrons, is observed also in

Au_2 (g).

In view of the apparent relation between bonding

in the gas phase and in the pure liquids, we have looked

for a relation between the dissociation energies of the

asymmetric molecules and the enthalpies of mixing. The

systems Cu-Ag-Au are relatively well suited for such a

comparison since the pure metals have the same crystal

structure and approximately the same radii. Furthermore

the alloys have well determined and relatively simple

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phase diagrams.

The enthalpies of mixing are shown in column 5 of Table V. There seems to be a qualitative relation between those enthalpies and deviation from Pauling's rule shown in column 4. AuCu has the largest deviation from Pauling's rule, and the largest excess enthalpy of mixing ; for AgAu both are smaller, and for AgCu, they are the smallest.

Activity data and dissociation energies are known for the system NaK where the deviation from Pauling's rule and the enthalpy of mixing both are very small.

Work is under way to extend the above relation.

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Table 1. Corrected dimer/monomer ratios and calculated dissociation energies from ion intensities above pure metals (Exp. 19 and 20) and alloys (Exp. 4, 10, 14, 16, 17).

(1) Exp.	(2) T·K	(3) $\frac{XY}{Y} \times 10^4$	(4) D_o^c kcal
Cu$_2$			
20	1549	6.20	43.46
	1634	9.93	43.43
	1642	9.67	43.14
	1709	13.82	43.12
	1620	7.94	42.95
	1582	7.15	43.30
		mean:	43.23
Ag$_2$			
19	1356	6.86	35.42
	1352	8.69	36.14
	1479	13.12	34.95
	1502	15.13	34.95
	1447	12.04	36.10
	1418	11.44	35.63
	1336	7.48	36.00
		mean:	35.70
Au$_2$(a)			
14	1666	10.46	52.09*
	1722	11.90	51.55*
	1803	18.66	52.25*
16	1734	15.89	52.67
	1742	14.15	52.23
	1703	7.81	50.86
	1658	10.30	52.58
	1777	13.17	51.32
17	1694	12.64	52.24*
	1778	15.67	51.62*
	1726	12.53	51.60*
		mean	51.91

(1) Exp.	(2) T·K	(3) $\frac{XY}{Y} \times 10^4$	(4) D_o^c kcal
AgAu(a)			
14	1568	3.73	48.17
	1575	3.22	46.32*
	1667	7.12	48.26*
	1722	8.90	47.92*
	1798	12.00	47.76*
17	1566	2.89	47.28
	1612	3.27	46.71*
	1694	6.58	47.51*
	1778	9.50	47.96*
	1726	9.34	47.86*
	1788	8.82	46.61
		mean:	47.58
AgCu(b)			
04	1484	1.78	41.56*
	1632	2.85	41.20
	1674	4.27	39.90
	1770	7.15	39.77
10	1565	5.16	42.76
	1583	3.01	40.66
		mean:	40.65
AuCu(a)			
16	1725	47.9	54.32
	1734	43.5	53.83
	1742	53.3	54.43
	1703	41.8	54.25*
	1658	47.3	55.39*
	1781	62.8	54.49*
	1798	74.1	54.81*
		mean:	54.50

(a) In experiments 14, 16, and 17 corrections of 0.3, 0.7, and 0.3 kcal respectively have been added to D_o to compensate for the reduced activity of gold in the alloys.

(b) 0.3 kcal has been added to D_o^o (AgCu) for the reduced activity of copper.

* average of 3 to 5 consecutive measurements at the same temperature.

TABLE II. Ionization cross sections and relative yield of the multiplier.

Species	ionization cross section	mult. yield x cross section
Cu	18.4	18.4
Cu_2	36.8	26.1
Ag	34.8	24.7
Ag_2	69.6	32.4
Au	35	16
Au_2	70	27
AgCu	53.2	29.3
AgAu	70	29.
AuCu	53	22

TABLE III. H_{298}^{vap} of gold (kcal).

Ruff and bergdahl (20 a) (1919)	82.98
Ruff and Konschak (20 b) (1926)	81.71
Harteck (20 c) (1928)	91.22
Farkas (20 d) (1929)	88.40
Baur and Brunner (20 e) (1934)	78.12
Hall (20 f) (1951)	84.70
Nesmaianov, Smakhtin, Lebedev (20 g) (1957)	87.70
Edwards (20 h) (1959)	87.20
Rauh (20 i) (1959)	87.50
Selected Average (last three values)	87.5

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TABLE IV. Dissociation energies at $0°$ K of Ib symmetric

and asymmetric molecules in kcal/mole.

	This work	Drowart Honig (4) recalc.	Schissel (5) recalc.	Spectr. (b.-S.)
Cu_2	43.2 ± 2.2	46.4 ± 2.3	43.9 ± 2.3	48
Ag_2	35.7 ± 2.2	37.8 ± 2.3	36.2 ± 2.3	42
Au_2	51.9 ± 2.2	53.0 ± 2.3	51.8 ± 2.4	62
$AgAu$	47.6 ± 2.2	-	-	-
$AgCu$	40.7 ± 2.2	-	-	29
$AuCu$	54.5 ± 2.2	-	-	64

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Table V. Comparison of D_o^O (XY) with $1/2 \left[D_o^O (X_2) + D_o^O(Y_2) \right]$

(Pauling's rule) and with the enthalpy of mixing

for the alloys.

Species	D_o^O exp. kcal	D_o^O calc. kcal		H^{mix} (liquid) n = 0.5
AgAu	47.6	43.8	+3.8 ± 1.7[*]	−1.1(1350°K)(22a)
AgCu	40.7	39.4	+1.3 ± 1.7[*]	0,8(1428°K)(22b)
AuCu	54.5	47.6	+6.9 ± 1.7[*]	−2.7(1550°K)(27)

[*] Most probable error including ± 1.4 kcal experimental error plus error in ΔH^{vap} (see text). This error is smaller than the uncertainties in the absolute values due to compensating errors.
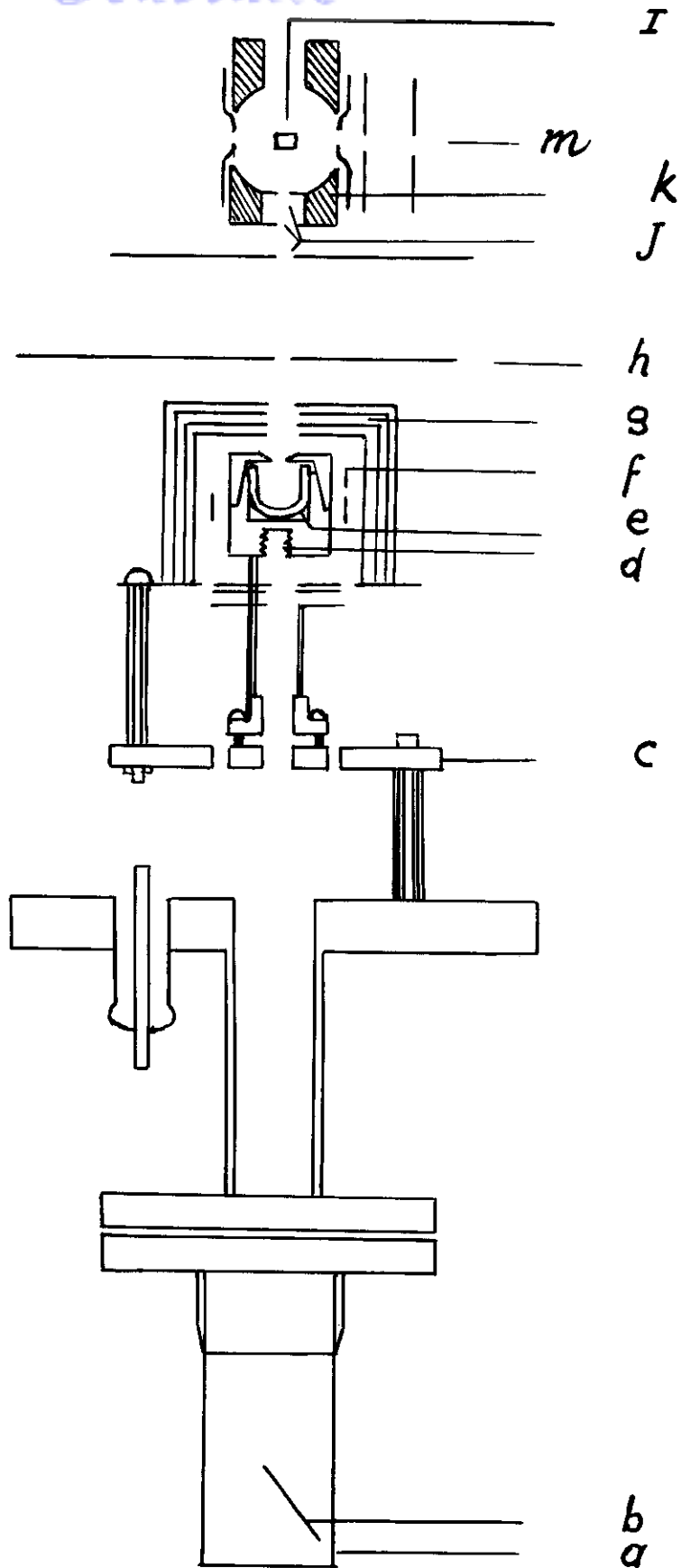
24

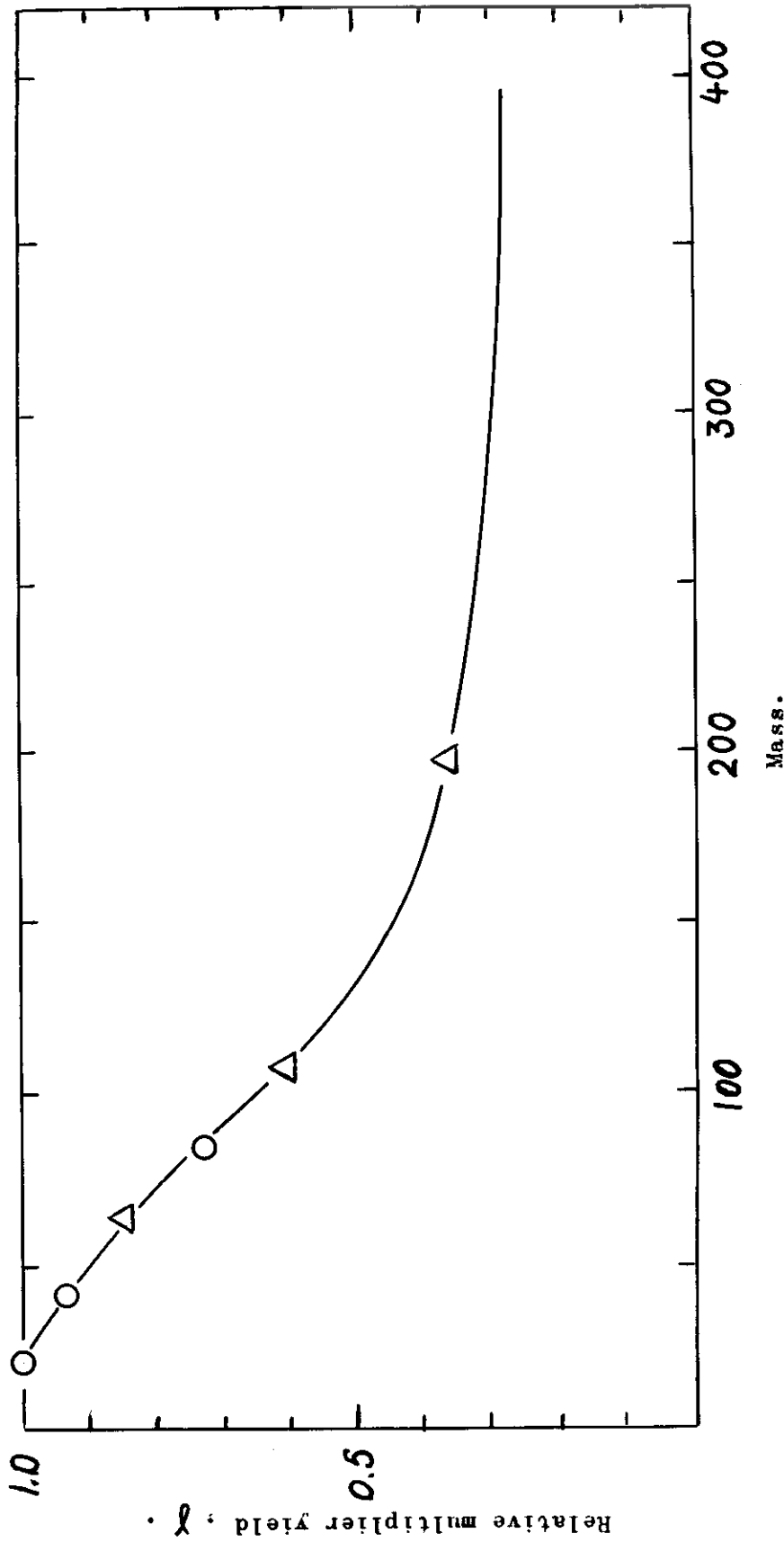Figure 1. Electron bombardment furnace and ion source

Figure 2. Relative yield as a function of mass for AgMg secondary electron multiplier with 4500 e.v. ions of rare gases (O) and Cu, Ag, and Au (△).