Mass-spectrometric Determination of the Dissociation Energy of the Molecule AuMn

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MASS spectrometry and optical spectroscopy have identified[1–4] several gaseous intermetallic molecules of gold. The search for some further species and the determination of their dissociation energies by mass spectrometry is hampered by the disparity in the vapour pressures of the elements. This difficulty can be circumvented by the use of compounds to reduce the pressure of the more volatile metal (Mn in this case), with the additional advantage that such a system is monovariant.

The molecule AuMn whose dissociation energy is reported here was so identified in the system $MnS(s) + Au(l)$, in which the other gaseous heteronuclear species are $MnS(g)$, $AuS(g)$, and $Au_2S(g)$.

The principle of the method and the experimental procedure have been described earlier.[2,5] For the present study a molybdenum Knudsen cell heated by electron bombardment was used.

The dissociation energy D_0^0 of the molecule AuMn was derived from the equilibrium constant K_p of the exchange reaction

$$AuMn(g) + Au(g) \rightarrow Mn(g) + Au_2(g) \qquad (1)$$

with the relation

$$\Delta H_0^0 = -\boldsymbol{R}T\ln K_p - T\Delta\,(G^0 - H_0^0)/T = D_0^0(AuMn) - D_0^0(Au_2)$$

The equilibrium constant (Table) was obtained directly as the product of the relative ion intensities of $AuMn^+$, Au^+, Mn^+, and Au_2^+ measured with 30 ev ionizing electrons. The assumption was thus made that the relative ionizing cross

Enthalpy change for the exchange reaction

$AuMn(g) + Au(g) \rightarrow Mn(g) + Au_2(g)$

T (°K)	log$K$	$-\Delta(G_0^0 - H_0^0)/T$ (cal. deg.$^{-1}$ mole^{-1})	$-\Delta H_0^0$ (kcal. mole^{-1})
1872	0·39[a]	3·34	9·5
1924	0·33	3·34	9·3
1930	0·35	3·34	9·5
1955	0·45	3·34	10·5
1956	0·47	3·34	10·7
1964	0·29	3·34	9·1
1970	0·29	3·34	9·1
1970	0·30	3·34	9·2
			average 9·6 ± 0·6

[a] Typical intensity ratios are: $I_{Mn}/I_{Au} = 2\cdot2$; $I_{Au_2}/I_{AuMn} = 1\cdot1$; $I_{Au}/I_{Au_2} = 6\cdot2 \times 10^2$.

sections and multiplier yields mutually compensate one another. The numerical values of the free energy functions $(G^0 - H_0^0)/T$ for Au(g) and Mn(g) were taken from the literature.[6] Those for Au_2 and AuMn were calculated from the usual statistical mechanical formulae with the experimental[3] vibration frequency $\omega_e = 190\cdot9$ cm.$^{-1}$, interatomic distance $r_e = 2\cdot472$ Å and electronic ground state $^1\Sigma$ for Au_2 and with the estimated values $\omega_e = 225$ cm.$^{-1}$, $r_e = 2\cdot35$ Å for AuMn. The electronic state of the latter molecule was assumed to be $^7\Sigma$ by analogy with MnH.[3] The numerical values are $-(G^0 - H_0^0)/T = 71\cdot58$ and 72·51 for Au_2 and 73·28 and 74·23 cal. deg.$^{-1}$ mole^{-1} for AuMn at 1800 and 2000° K respectively.

The dissociation energy of the molecule Au_2, $D_0^0(Au_2) = 53\cdot0 \pm 2$ kcal./mole is that determined earlier,[7] recalculated for the interatomic distance given above (rather than the estimated $r_e = 2\cdot68$ Å) and for relative ionization cross sections $\sigma_2/\sigma_1 = 1\cdot5$ (rather than 2 used previously), taken by analogy with measurements for a number of diatomic molecules.[2]

The reaction enthalpy $\Delta H_0^0(1) = -9\cdot6 \pm 0\cdot6$ kcal./mole thus yields $D_0^0(AuMn) = 43\cdot4 \pm 3\cdot0$ kcal./mole.

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[1] J. Drowart in "Phase Stability in Metals and Alloys", ed. P. S. Rudman, J. Stringer, and R. I. Jaffee, McGraw-Hill, New York, 1967, p. 305.
[2] J. Drowart and P. Goldfinger, *Angew. Chem.*, 1967, **79**, 589; *Angew. Chem. Internat. Edn.*, 1967, **6**, 581.
[3] C. J. Cheetham and R. F. Barrow, *Adv. High Temp. Chem.*, *Vol.* 1, Academic Press, New York, 1967, p. 7.
[4] A. Kant, private communication.
[5] M. G. Inghram and J. Drowart in "High Temperature Technology", McGraw-Hill, New York, 1960, p. 219.
[6] D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements", *Adv. Chem. Series* 18, American Chemical Society, Washington, D.C., 1956.
[7] M. Ackerman, F. E. Stafford, and J. Drowart, *J. Chem. Phys.*, 1960, **33**, 1784.