

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

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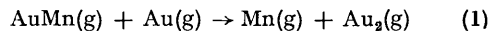
Mass spectrometry and optical spectroscopy have identified¹⁻⁴ several gaseous intermetallic molecules of gold. The search for some further species and the determination of their dissociation energies by mass spectrometry is hampered by the disparity in the vapour pressures of the elements. This difficulty 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 $\text{MnS(s)} + \text{Au(l)}$, in which the other gaseous heteronuclear species are MnS(g) , AuS(g) , and $\text{Au}_2\text{S(g)}$.

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° of the molecule AuMn was derived from the equilibrium constant K_p of the exchange reaction

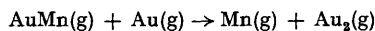


with the relation

$$\Delta H_0^\circ = -RT \ln K_p - T \Delta (G^\circ - H_0^\circ)/T = D_0^\circ(\text{AuMn}) - D_0^\circ(\text{Au}_2)$$

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



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: $I_{\text{Mn}}/I_{\text{Au}} = 2.2$; $I_{\text{Au}_2}/I_{\text{AuMn}} = 1.1$; $I_{\text{Au}}/I_{\text{Au}_2} = 6.2 \times 10^2$.

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 Au₂ and AuMn were calculated from the usual statistical mechanical formulae with the experimental³ vibration frequency $\omega_e = 190.9$ cm.⁻¹, interatomic distance $r_e = 2.472$ Å and electronic ground state $^1\Sigma$ for Au₂ and with the estimated values $\omega_e = 225$ cm.⁻¹, $r_e = 2.35$ 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 $-(G^0 - H_0^0)/T = 71.58$ and 72.51 for Au₂ 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 Au₂, $D_0^0(\text{Au}_2) = 53.0 \pm 2$ kcal./mole is that determined earlier,⁷ recalculated for the interatomic distance given above (rather than the estimated $r_e = 2.68$ Å) and for relative ionization cross sections $\sigma_2/\sigma_1 = 1.5$ (rather than 2 used previously), taken by analogy with measurements for a number of diatomic molecules.²

The reaction enthalpy $\Delta H_0^0(1) = -9.6 \pm 0.6$ kcal./mole thus yields $D_0^0(\text{AuMn}) = 43.4 \pm 3.0$ kcal./mole.

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