Chemistry. — *On the Law of Additive Atomic Heats in the Case of Intermetallic Mixed Crystals. X. Silver and Gold.* By J. A. BOTTEMA and F. M. JAEGER.

(Communicated at the meeting of September 24, 1932).

§ 1. After the experience hitherto gathered [1]) in studying the deviations from the so-called law of additive atomic heats in chemical compounds between metals, it appeared of interest to extend these investigations also to mixed crystals. In the present paper an alloy of *gold* and *silver*, consisting of mixed crystals, was investigated by us with the purpose of verifying the presence and the order of magnitude of the deviations from the rule of additive atomic heats in such a case of the formation of mixed crystals between two metallic components. As is well known, *silver* and *gold* yield an uninterrupted series of mixed crystals, ranging from 0—100 % of the two components. The special alloy here studied contained 22.456 grammes of *gold* and 35.766 grammes of *silver*; the total weight of the sample was, therefore, 58.222 grammes. This corresponds to a mixture of 25.56 at. % Au and 74.44 at. % Ag; the composition of the mixed crystal being, therefore, equivalent to: $Ag_3\,Au_{1.0387}$, which involves an apparent "molecular weight" of: 531.14.

The quantities of heat Q_0 developed in the different calorimetric experiments are given in Table I.

TABLE I.

N⁰. of Exp.:	Temperature t in °C.:	Final temp. t' of Calorimeter:	Heat developed Q between t and t':	Heat developed Q_0 between t and 0°:	Q'_0 as calculated from the formula:
6	100°.03	21°.63	3.6135	4.6134	—
1	234.37	20.96	9.9910	10.9599	10.9748
5	310.65	21.72	13.6981	14.7021	14.6905
10	348.28	21.31	15.6586	16.6437	16.5428
2	394.3	21.40	17.9516	18.9408	18.8307
9	431.73	21.89	19.7582	20.7701	20.7079
8	466.43	21.53	21.4975	22.4907	22.4626
7	509.5	22.19	23.6347	24.6605	—
3	629.43	21.63	29.9040	30.9039	30.8890
4	800.77	22.59	39.0255	40.0698	—

[1]) F. M. JAEGER and J. A. BOTTEMA, these Proceedings, **35**, (1932), 352 and the previous paper.

These quantities of heat Q_0 can sufficiently well [1]) be represented by means of the equation:

$$Q_0 = 0.0455677 \,.\, t + 0.05514.10^{-4} \,.\, t^2 + 0.08879.10^{-9} \,.\, t^3$$

and c_p, therefore, by:

$$c_p = 0.0455677 + 0.11028.10^{-4} \,.\, t + 0.26637.10^{-9} \,.\, t^2.$$

With the same order of exactness (1.5 — 5 pro mille) the values of Q_0 can also be represented by the linear function:

$$Q_0 = 0.04561 \,.\, t + 0.05559.10^{-4} \,.\, t^2$$

and c_p, therefore, by:

$$c_p = 0.04561 + 0.1118.10^{-4} \,.\, t.$$

The true specific heats c_p and the corresponding "molecular" heats C_p are, for a series of temperatures, calculated according to the latter formula and the values obtained are in Table II compared with the sum Σ of the atomic heats of the components.

TABLE II.

Temperature t in °C.:	Specific Heats c_p observed:	'Molecular' Heats C_p observed:	Sum Σ of the atom. Heats of the Components:	Difference (Σ-C_p) in percentages:
100°	0.04693	24.926	24.942	+ 0.14 %
200	0.04785	25.415	25.475	+ 0.24
300	0.04896	26.005	26.000	— 0.02
400	0.05008	26.599	26.513	— 0.32
500	0.05120	27.195	27.012	— 0.67
600	0.05232	27.789	27.500	— 1.05
700	0.05344	28.384	27.979	— 1.44
800	0.05455	28.973	28.463	— 1.79

For *silver* and *gold* the values of the atomic heats C_p were calculated from the formulae previously [2]) given by us for the molten, solidified and stabilized metals.

The data of Table II prove, that even in the case of mixed crystals, there are *small* deviations from the rule of additive atomic heats, which

[1]) The greater deviations between the values observed and calculated occur between 250° and 450° C., because of the fact, that within this interval of temperatures the curve of the mean specific heats $\bar{c}_p$ in function of t shows a change of its curvature which proves to be a real one. The deviations are, however, not greater than about 0.5 %; the major part of the curve, more particularly at higher temperatures, is almost a straight line.

[2]) F. M. JAEGER, E. ROSENBOHM and J. A. BOTTEMA, these Proceedings, **35**, (1932), 763, 772.

clearly increase with augmenting temperatures. But these deviations are, for the greater part, *so small, that they remain within the limits of the uncertainties of the calculation itself;* only at temperatures surpassing 600° C. they become somewhat greater. In this respect, the mixed crystal certainly behaves differently from the true intermetallic compounds hitherto studied.

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Astronomy. — *Mittlere Lichtkurven von langperiodischen Veränderlichen.* VIII. *R Leonis minoris.* Von A. A. NIJLAND.

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Instrumente: *S* und *R*. Die Beobachtungen wurden alle auf *R* reduziert: die Reduktion *R*—*S* beträgt —0^m.35. Spektrum M7—8e (*Harv. Ann.* 79 S. 170). Gesamtzahl der hier zu besprechenden Beobachtungen 592, von 2416836 bis 2426791). Der Stern ist von Mitte Juni bis Mitte August nicht beobachtbar, und die Lichtkurve (s. Fig. 1) zeigt Lücken, welche den Kurvenzug des öfteren unsicher machen und überdies die Gesamtzahl der Schätzungen von etwa 27 pro Jahr auf 22 herabdrücken.

Karte: HAGEN, *Atlas Stell. var. Series III.*

Die Stufenskala bezieht sich auf die Helligkeit 10^{m}0. Die Vergleichsterne sind in *Harv. Ann.* 29 schwer zu identifizieren, da die Koordinaten hier sehr ungenau angegeben sind. Die Helligkeit 10^m.86 für *k* fällt ganz aus der Skala heraus und blieb unberücksichtigt.

Nach MITCHELL (*Mem. Am. Ac.* **14**, IV, 284) bezieht sich die Helligkeit 12^m.97 aus *Harv. Ann.* 74 auf Stern *m*; ganz sicher ist das allerdings nicht, da die Koordinaten nur in Zehnteln Bogensekunden und ganzen Bogenminuten gegeben sind. Nach *Harv. Ann.* 37 wäre vielleicht *n* wahrscheinlicher. Die Grössen der *Harv. Ann.* 94 sind scheinbar den *Harv. Ann.* 37 entnommen; Stern *b* wird aber als 7^m.94 gegeben. Die Grössen von MITCHELL findet man a. a. O.

Stern *j* wurde fünf-mal, entweder direkt oder mittels des schwächeren Sterns *k*, an die Grenze 11^m.60 des Suchers *S* angeschlossen; das Mittel der schlecht stimmenden Resultate ist 11^m.11. Es ist kaum anzunehmen, dass der Stern viel schwächer wäre, denn tatsächlich habe ich den Stern *k* zweimal ganz bequem im Sucher sehen können. Vielleicht liegt in den *Harvard*-Grössen ein systematischer Fehler vor. Ich habe mich schliesslich an die Skala der *HP* gehalten. Der Stufenwert wird dann 0^m.101; tatsächlich hat dabei die nur 6-mal beobachtete Differenz *np* nicht mitgestimmt.

Es liegen 104 Schätzungen der Farbe vor, welche aber für vier