

obtained with the same materials under different conditions and by independent observers. The experience hitherto gathered, has already proved the perfect reproducibility of the values obtained under similar conditions and the soundness of the method employed, yielding an exactness of the respective data of 0.1 or 0.2 %.

*Groningen, Laboratory for Inorganic and Physical
Chemistry of the University.*

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances between 0° and 1625° C. VI. On the Law of NEUMANN-JOULE-KOPP-REGNAULT concerning the Molecular Heat of Chemical Compounds in Function of the Atomic Heats.* By F. M. JAEGER and J. A. BOTTEMA.

(Communicated at the meeting of April 2, 1932.)

§ 1. By a series of experimental investigations of NEUMANN¹⁾ (1831), REGNAULT²⁾ (1840), JOULE³⁾ (1844), KOPP⁴⁾ (1864), PAPE⁵⁾ (1864) and others, it seemed finally to be proved, that the molecular heat-capacity of a chemical compound can be calculated from the atomic heats of its composing atoms in a simple "additive" way. This law is commonly expressed by saying, that the atoms preserve their individual, normal specific and atomic heats also in their combinations with each other. MEYER⁶⁾ first proved that the law is only an approximate one, calculation and experiment agreeing the better, the more the molecular volume approaches the sum of the atomic volumes, a conclusion contested by VAN AUBEL⁷⁾. In recent times occasionally doubt has arisen about the validity of the law. By comparison of the specific heats of the pure elements with those of their compounds, SCHIMPF⁸⁾ and SCHÜBEL⁹⁾ tried to demonstrate, that deviations are present in the case of intermetallic compounds. SCHÜBEL, for instance, accepts the rule as an approximate one; he finds positive, as well as negative deviations, in most cases of no more than about 2 %, occasionally of 6 %, and independent of the temperature.

Recently TAMMANN and ROHMANN¹⁰⁾ have again taken up the subject; they find, by comparison of the data in literature of the quantities of heat

1) F. E. NEUMANN, Pogg. Ann. d. Phys., **23**, (1831), 32.

2) H. V. REGNAULT, Ann. de Chim. et Phys., (2), **73**, (1840), 5; (3), **1**, (1841), 129; (3), **9**, (1843), 322; Pogg. Ann. d. Phys., **51**, (1840), 44, 213; **53**, (1841), 60, 243; **62**, (1844), 50.

3) J. P. JOULE, Phil. Mag., (3), **25**, (1844), 334.

4) H. KOPP, Lieb. Ann. d. Chem., Suppl. **3**, (1864), 1; (1865), 290, 301.

5) C. PAPE, Pogg. Ann. d. Phys., **120**, (1863), 337, 579; **122**, (1864), 408; **123**, (1864), 277.

6) S. MEYER, Wien. Sitzb. **109**, (1901), 405; Drude's Ann. d. Phys., **2**, (1900), 135.

7) E. VAN AUBEL, Journ. de Phys., (3), **10**, (1901), 36.

8) H. SCHIMPF, Zeits. f. phys. Chem., **71**, (1910), 257.

9) P. SCHÜBEL, Zeits. f. anorg. Chem., **87**, (1914), 81, 101, 109.

10) G. TAMMANN und A. ROHMANN, *ibid*, **190**, (1930), 227.

developed, for the free elements and a number of intermetallic compounds positive as well as negative discrepancies, independent of temperature, and evidently connected with the diminution or increase of the specific volume of the compound in comparison with the sum of the atomic volumes of the constituting elements.

However, since we were able to demonstrate, that even where no allotropism of the metals investigated occurs, reproducible values of \bar{c}_p can, with metals, only be obtained, if they really are *stabilized* (see next paper), and that a great number of the data on \bar{c}_p and c_p published in literature only correspond to *undefined* states of these metals, — it must be evident, that such a comparison has no significance as a decisive proof, as long as the data of c_p , and especially their variation with the temperature, are so uncertain as they are just now. Such a comparison is only possible, if the following conditions are fulfilled :

1⁰. The c_p - t -curves of the components and of the compounds must be determined by the same observers with the greatest possible accuracy and then the obtained numbers be compared for each temperature.

2⁰. Proof must be given that the numbers thus measured are perfectly reproducible and that they really correspond to the normal, stabilized condition of the objects investigated.

3⁰. The method used in determining the integral heat-quantities must be so reliable, that no errors surpassing a few tenths of a percent, even at the highest temperatures, can occur.

4⁰. Thorough tests by means of *X-ray-analysis* must insure the exclusive presence of either the pure components or of the real compound to be studied, without mixed crystals or admixtures of the free elements being any longer present. The method developed in this laboratory is now so improved and perfected, that the values of \bar{c}_p obtained in favourable cases are certain within 0.1 or 0.2 %. In this way the determination of the specific heats in their dependence on the temperature, has become one of the most sensitive methods of discovering changes in the behaviour and in the internal condition of such metals. The problem about the validity of the law mentioned, therefore, was taken up by us some time ago ; in this paper the first results obtained will be communicated.

§ 2. *Tin*. The mean specific heat of *tin* was determined by means of a lump of the purest ¹⁾ *tin*, which was carefully melted and cast into the form of the usual vacuum crucibles, fitting exactly in the central opening of the calorimeter ; then it was slowly cooled. The piece of *tin* thus obtained was suspended by means of a little hook made of silver ; the lump of *tin* weighed 91.1967 Gr., the silver hook 0.5393 Gr. The thermoelement used was carefully calibrated at the boilingpoint of water under known pressure

¹⁾ Purest tin from E. MERCK; for the mean specific heat between 20° C. and 0° C. the value: **0.0538** has been used in the calculation of the small correction for Q_0 .

(99°.964 C.), at the meltingpoint of tin (231°.84 C.) and at the melting-point of potassiumdichromate (397°.5 C.). With respect to the standard-couple compared with the nitrogengasthermometer-scale of DAY and SOSMAN, the deviations of this thermocouple were: at 100° C.: — 3.4 M.V.; at 150° C.: — 1.8 M.V.; at 190° C.: — 0.4 M.V.; at 220° C.: + 0.8 M.V.; at 231°.84 C.: + 1.1 M.V. These values proved to be in full accordance with the other corrections of the values of its thermoelectric force, as measured up to 1540° C.

The total amounts of heat delivered by 1 Gr. of *tin* between t^0 and 0° C. were found to be :

Temperature t in 0° C.:	Total Amount of Heat Q_0 developed between t^0 and 0° C. in calor.:
100.215	5.5246
100.514	5.5492
100.584	5.5453
100.600	5.5672
151.00	8.4492
154.40	8.6282
190.166	10.7650
190.96	10.8061
218.60	12.5243
219.80	12.6380

As *tin* shows an allotropic change at 203° C., the last numbers correspond to the rhombic modification; indeed, they are about 10 % higher, than they would be calculated by extrapolation for the tetragonal modification. From the values: 100°.478 and 5.5466 cal.; 151° and 8.4492 cal., and 190°.563 and 10.7856 cal., the following formula for Q'_0 was calculated:

$$Q'_0 = 0.05393 \cdot t + 0.111425 \cdot 10^{-4} \cdot t^2 + 0.15037 \cdot 10^{-7} \cdot t^3,$$

which equation is valid between 0° and 203° C., because, on cooling, the transformation-point at 13° C. is passed, without an allotropic change taking place.

From this c_p is calculated to be :

$$c_p = 0,05393 + 0,22285 \cdot 10^{-4} \cdot t + 0,45111 \cdot 10^{-7} \cdot t^2.$$

The true specific heat of the white, tetragonal (metastable) *tin* at 0° C., would, therefore, be: 0.05393. This number is in perfect agreement with BRÖNSTED'S directly measured value¹⁾: 0.05382.

¹⁾ J. N. BRÖNSTED, Zeits. f. phys. Chem., **88**, (1914), 479. The true specific heat c_p of grey, cubic tin at the same temperature is smaller: **0.0496**, according to this author.

The atomic heat C_p of tetragonal *tin* between 0° or 13° and 203° C. can thus be calculated from the formula :

$$C_p = 6,4014 + 0,26454 \cdot 10^{-2} \cdot t + 0,53546 \cdot 10^{-5} \cdot t^2.$$

Temperature in 0° C. :	Atomic Heat C_p :
0	6.4014
20	6.4564
50	6.5470
100	6.7195
150	6.9187
190	7.0973
200	7.1447
232	7.3033 (extrap.)

IITAKA ¹⁾ has determined the specific heat of *solid, rhombic tin* at 232° C. and that of *liquid tin* at the same temperature. The first value, represented by the point C in Fig. 1 proves to be somewhat greater than that indicated by the point B, which, for a temperature of 203° C., follows from the amount of heat delivered at that temperature, as calculated from the corresponding values at $218^\circ.6$ and at $219^\circ.8$ C. This means, that the atomic and specific heats of *a-tin* ²⁾ vary with the temperature in the way

Atomic Heat C_p
in calories

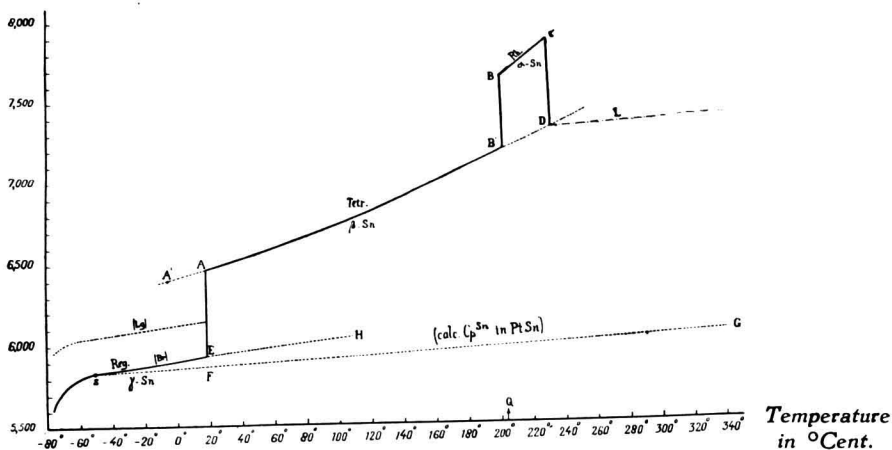


Fig. 1

¹⁾ I. IITAKA, Science Rep. Tohoku Univ., 8, (1919), 99.

²⁾ The transformation-temperature: tetragonal \rightleftharpoons rhombic tin lies at $202^\circ.8$ C., according to A. SMITS and H. L. VAN DER LEEUW, these Proceed., 15, (1912), 681.

indicated in Fig. 1. His second value, — that for liquid tin, — is just the same, as the *extrapolated* value: 7.303 at 232° C., which follows from our own C_p - t -curve. Moreover, from PIONCHON's¹⁾ measurements of the specific heat of liquid tin between 250° and 1100° C., at least the temperature-coefficient of c_p for liquid tin can approximately be deduced: it is very small, about 0.00105 for every 50°. If we start from the point D , the coefficient corresponding to C_p approximately gives the direction of the curve L in Fig. 1. Finally, BRÖNSTED (loco cit.) has measured the true specific heats of grey tin: from these values the curve of the atomic heats of γ -tin is constructed. In this way the complete diagram, as represented in Fig. 1, can be deduced²⁾.

§ 3. The compound: PtSn.

The specific heats of *platinum* and of *tin* now being exactly known, we have, — as a first example of a homopolar compound of two metals, — chosen the compound: $PtSn$. While *platinum* is cubic, *tin* either cubic, tetragonal or rhombic, the compound $PtSn$ is hexagonal and its existence, therefore, easily controlable by means of X -ray analysis. While the *white tin* has tetragonal symmetry, with: $a_0 = 5.83 \text{ \AA}$., $c_0 = 3.16 \text{ \AA}$ and $N = 4$, or, — which is equivalent to this, —: $a'_0 = 8.23 \text{ \AA}$., $c'_0 = 3.16 \text{ \AA}$., with $N' = 8$ and a diamond-like structure, which is compressed in the direction of the c -axis, — the *grey tin* is cubic, with $a_0 = 6.46 \text{ \AA}$., and $N = 4$. The smallest distance of two Sn -atoms in grey tin is: 2.80 \AA ., — a value which is quite comparable with that found in the case of *platinum*: 2.78 \AA . Platinum is cubic, with a face-centred cell and $a_0 = 3.912 \text{ \AA}$.; $N = 4$ atoms pro cell. The compound $PtSn$ (see Table I) is hexagonal, has the same type of structure as $NiAs$, and contains 2 molecules, i.e. the mass: Pt_2Sn_2 pro cell. Its density at 0° is: 13.1.

The compound $PtSn$, enclosed in a platinum vacuum crucible of the usual form (30.1341 Gr.) weighed 25.7467 Gr. Its chemical analysis yielded: 37.78 % Sn and 62.22 % Pt ; the theoretical values are: 37.81 % Sn and 62.19 % Pt . An X -ray analysis by means of the powder-method gave the results collected in Table I.

¹⁾ J. PIONCHON, Ann. de Chim. et Phys., (6), **11**, (1887), 33.

²⁾ No more reliable values of c_p for grey tin than these are, as far as we know, available at this moment. The values determined by F. LANGE, Zeits. f. phys. Chem., **110**, (1924), 343, (dotted line Lg in Fig. 1) are somewhat higher than those of BRÖNSTED (loco cit.) and the number of both authors have been criticized by E. COHEN and A. L. TH. MOESVELD. Those of BRÖNSTED seem to be more reliable than LANGE's data.

However, this does not make much difference for our purpose, as they are certainly appreciably lower than those for β -tin; our conclusion, that the values of C_p for tin in $PtSn$ must be nearer to those of γ -, then to those of β - (and α -, or liquid tin), remains, therefore, in all cases quite justified. The transition-point: γ -tin \rightleftharpoons β -tin lies at 13° C.; conf. E. COHEN and Collab., Zeits. f. phys. Chem., **30**, (1899), 601; **33**, (1900), 57; **35**, (1900), 588; etc. Recent measurements yield 13° C. (COHEN).

TABLE I.
Powder-Spectrogram of the Compound $Pt Sn$ (tempered at $400^\circ C.$)
(Crucible: 24).

No. of Line:	$2l$ in m.M.:	Estim. Intens.:	Wave-length λ :	Angle θ :	$\text{Sin}^2 \theta$ (observed):	$\text{Sin}^2 \theta$ (calculated):	Indices (hkl):
1	45.4	1	β	$11^\circ 21'$	0.0387	0.0383	(100)
2	50.4	4	"	12 36	0.0476	0.0469	(100)
3	54.3	1	β	13 34	0.0551	0.0548	(101)
4	60.2	4	"	15 3	0.0674	0.0670	(101)
5	75.4	3	β	18 51	0.1044	0.1040	(102)
6	79.4	3	"	19 51	0.1156	0.1149	(110)
7	83.8	10	"	20 57	0.1278	0.1272	(102)
8	88.4	8	"	22 6	0.1415	0.1407	(110)
9	97.2	1 ?	β	24 18	0.1694	0.1694	(201) ?
10	102.9	1	"	25 43	0.1884	0.1875	(200)
11	108.9	1	"	27 14	0.2093	0.2076	(201)
12	111.9	2	β	27 58	0.2200	0.2184	(202)
13	114.0	1	"	28 30	0.2277	0.2278	(103)
14	124.9	4	"	31 14	0.2687	0.2679	(202)
15	138.1	1	"	34 31	0.3212	0.3216	(203) or (113)
16	140.2	1	"	35 3	0.3298	0.3281	(210)
17	141.3	1	β	35 20	0.3343	0.3342	(212)
18	144.6	1	"	36 9	0.3480	0.3482	(211)
19	149.6	1	"	37 24	0.3689	0.3684 or 0.3685	(203) or (204)
20	151.7	1	β	37 55	0.3777	0.3780	(114)
21	159.2	5	"	39 48	0.4100	0.4086	(212)
22	162.6	2	"	40 39	0.4243	0.4220	(300)
23	171.2	5	"	42 48	0.4616	0.4625	(114)
24	182.4	2	"	45 36	0.5105	0.5090 or 0.5091	(213) or (204)
25	191.5	1	"	47 52	0.5500	0.5494	(105)
26	198.7	5	"	48 41	0.5639	0.5625	(220)
27	205.5	1	"	51 22	0.6104	0.6090	(310)
28	210.1	1	" (β)	52 32	0.6298	0.6291 or 0.6295	" (311) or β (106) and (401)
29	214.7	1	"	53 40	0.6498	0.6497	" ₁ (214)

TABLE I. (Continued).
 Powder-Spectrogram of the Compound *Pt Sn* (tempered at 400° C.)
 (Crucible : 24).

No. of Line:	2l in m.M.:	Estim. Intens.:	Wave-length λ :	Angle θ :	$\text{Sin}^2 \theta$ (observed):	$\text{Sin}^2 \theta$ (calculated):	Indices (hkl):
30	224.9	5	α	56° 14'	0.6893	0.6900	(205)
31	234.0	1	α (β)	58 15	0.7231	0.7232	α (006) or β (224)
32	238.3	5	α_1	59 34	0.7432	0.7434	α_1 (223)
33	239.1	1	α_2	59 47	0.7466	0.7436	α_2 (304) or β (321) and (206)
34	244.9	4	α_1	61 14	0.7682	0.7701	α_1 (106)
35	245.8	2	α_2	61 27	0.7716	0.7705	α_2 (401)
36	251.5	2	α (β)	62 52	0.7921	0.7982	α_2 (313) or β (322)
37	255.2	1	β	63 48	0.8050	0.8069	β (322)
38	263.0	5	α_1	65 45	0.8314	0.8304 or 0.8284	α_2 (402) or α_1 (215)
39	264.1	3	α_2	66 2	0.8348	0.8331	α_2 (215)
40	271.9	1	α_1	67 59	0.8584	0.8616	α_1 (116)
41	280.5	5	α_1	70 7	0.8845	0.8841	α_1 (224)
42	281.6	3	α_2	70 24	0.8876	0.8868	α_2 (224)
43	289.8	5	α_1	72 27	0.9091	0.9111	α_1 (321)
44	291.4	3	α_2	72 51	0.9131	0.9136	α_2 (206)
45	299.3	5	α_1	74 50	0.9315	0.9304	α_1 (403)
46	301.2	3	α_2	75 18	0.9356	0.9339	α_2 (314)
47	321.7	8	α_1	80 25	0.9723	0.9683	α_1 (322)
48	325.3	6	α_2	81 20	0.9772	0.9742	α_2 (322)

Radius of Camera: 57.2 m.M. Exposure: 70 m. Amp. hours.

Wave-length: $\lambda_\alpha = 1.540 \text{ \AA}$; $\lambda_\beta = 1.388 \text{ \AA}$; $\lambda_{\alpha_1} = 1.5374 \text{ \AA}$; $\lambda_{\alpha_2} = 1.5412 \text{ \AA}$.

Quadratic Equation:

$$\sin^2 \theta = 0.04696 (h^2 + k^2 + hk) + 0.020125 \cdot l^2 \dots \dots \dots (\alpha)$$

$$\sin^2 \theta = 0.03815 (h^2 + k^2 + hk) + 0.016345 \cdot l^2 \dots \dots \dots (\beta)$$

Parameters of the Lattice: $a_0 = 4.103 \text{ \AA}$; $c_0 = 5.428 \text{ \AA}$.

Specific Weight: 13.09 Hexagonal; 2 molecules pro cell.

For the α_1 -ray, the coefficients of the quadratic equation are: 0.04680 and 0.020045; for the α_2 -line: 0.04703 and 0.020155 respectively.

By these data, — which were the same for the substance tempered at 400° C. and for the non-tempered substance, — it is proved that really

the hexagonal *compound* is present; it is identical with that studied in 1928 by OFTEDAHL¹⁾. No lines indicating either the presence of free platinum, or of free tin, were ever observed in the spectrograms.

§ 4. As the meltingpoint²⁾ lies in the vicinity of 1281° to 1330° C., the mean specific heats can be determined over a considerable range of temperatures. At temperatures lower than 400° C., the accuracy of the determinations is, as a consequence of the predominant quantity of the platinum present, somewhat less than at higher temperatures; but the extreme precision of the experimental method gives us a guarantee, that also at 189° and 222° C. the data of c_p obtained possess a fair degree of accuracy. Indeed, the very flat curve, — almost a straight line, — joining the values of Q between 418° and 1045° C., equally passes through the other points in the graph representing Q_0 in function of t , even at the lower temperatures.

The small corrections of Q for the heat given off between the final temperature t' of the calorimeter and 0° C. were calculated by adopting the value 0.0398 for the mean specific heat of the substance within the interval from 20° to 0° C.; this certainly is very close to the truth.

Temperature t in ° C. :	Total Amount of Heat Q_0 between t and 0° C. in calor. :	Q'_0 as calculated from the formula :
189.74	7.3728	—
221.88	8.6419	8.6408
418.67	16.5282	16.5324
644.90	25.8917	—
718.30	28.9991	28.9982
802.06	32.5927	32.5867
1044.80	43.2606	—

These quantities of heat Q_0 can be expressed in function of t by the formula :

$$Q'_0 = 0,03836 \cdot t + 0,25362 \cdot 10^{-5} \cdot t^2 + 0,0359597 \cdot 10^{-8} \cdot t^3,$$

and the specific heats of $PtSn$, therefore, by :

$$c_p = 0,03836 + 0,50724 \cdot 10^{-5} \cdot t + 0,107879 \cdot 10^{-8} \cdot t^2.$$

¹⁾ I. OFTEDAHL, Zeits. f. phys. Chem., **132**, (1928), 213.

²⁾ F. DOERINCKEL, Zeits. f. anorg. Chem., **54**, (1907), 349; N. PODKOPAJEW, Journ. russ. phys.-chem. Ges., **40**, (1908), 249. Nach dem letztgenannten Autor liegt der Schmelzpunkt etwa bei 1330° C.

As the molecular weight of $PtSn$ is 313.93, the molecular heat C_p' of the compound can be calculated from the equation :

$$C_p' = 12,0422 + 0,15924 \cdot 10^{-2} \cdot t + 0,33866 \cdot 10^{-6} \cdot t^2.$$

By means of this formula the values collected in Table II were obtained ; simultaneously the values of C_p for pure *tin* and *platinum* at the same temperatures are, for the purpose of comparison, also given in Table II.

Temperature in 0° C.	Atomic Heat of Tin (obs.):	Atomic Heat of Platinum (obs.):	Sum Σ :	Molecular Heat of $PtSn$ (obs.):	Difference in calories:	Percentage defic. of Σ :
20	6.452	6.197	12.649	12.074	0.575	4.54 %
30	6.481	6.209	12.690	12.090	0.600	4.73
40	6.513	6.221	12.734	12.107	0.627	4.92
50	6.546	6.233	12.779	12.123	0.656	5.13
60	6.575	6.245	12.820	12.139	0.681	5.31
70	6.610	6.257	12.867	12.156	0.711	5.53
80	6.641	6.269	12.910	12.172	0.738	5.71
90	6.682	6.281	12.963	12.189	0.774	5.97
100	6.717	6.293	13.010	12.205	0.805	6.18
120	6.791	6.317	13.108	12.239	0.869	6.63
140	6.870	6.341	13.211	12.272	0.939	7.17
160	6.957	6.365	13.322	12.306	1.016	7.63
180	7.049	6.389	13.438	12.341	1.097	8.16
200	7.141	6.414	13.555	12.375	1.180	8.70

From these data it at once becomes clear, that the molecular heat of the compound $PtSn$ is, at each temperature, *appreciably less than the sum of the atomic heats of the composing elements*, as observed at the same temperatures: the differences are 50 to 80 times as great, as the total experimental errors of the measurements.

There cannot be the least doubt, therefore, that the NEUMANN-JOULE-KOPP-REGNAULT-law is *not valid*: the differences range from 4.5 to 8.7 % of the additive values. Most remarkable is the fact, *that these differences are themselves a function of the temperature*; on a first approximation they increase linearly with the temperature.

The curve *FG* in Fig. 1 represents the values of C_p for *tin* in the compound, as calculated if it is supposed that the values of C_p for *platinum* in the compound are really preserved, — which certainly is *not* very probable, — as these, too, will be diminished to some extent.

The curve *FG* lies very close to the *extrapolated* curve *EH* for the *grey tin* (intersecting this curve at about -50° C.). If it is assumed, that the values of C_p for *platinum* in *PtSn* are equally different from those of the free element and are themselves also somewhat diminished (by about 0.05 to 0.10 calories), the curve *FG* would still be shifted a little upwards, in such a way, that it would practically coincide with the (extrapolated) curve for *grey tin* in the metastable condition. It is obvious, that the calculated values of C_p for *tin* in the compound, do *not* manifest ¹⁾ the discontinuities, characteristic of the allotropic transformations of pure tin; moreover, that these values doubtlessly very closely approach the extrapolated values for (metastable) *grey tin*. In this connection attention may also be drawn to the specific volumes of the compound and its components: as the specific weight of *PtSn* is 13.091 at 0° C. (2 mol. pro cell), that of *Pt* (4 atoms pro cell) 21.23 at the same temperature, and that of *grey tin* ²⁾ 5.751 at 18° C. (4 atoms pro cell), the rule of additive volumes would require:

$$2 \left(\frac{195.23}{d_{Pt}} + \frac{118.7}{d_{Sn}} \right) = \frac{313.93}{d_{PtSn}},$$

or: $2(9.19 + 2.06) = 24$. Actually the first member of this equation is: 23. This means, that the specific volume of the compound is a little greater (4%) than the sum of the volumes of both components. If, in stead of the specific weight of *grey tin*, that of *white* (tetragonal) tin was used

¹⁾ If the values for pure *platinum* between 0° and 1275° C. are subtracted from the observed molecular heats of *PtSn*, as deduced from the experimental data, the following (virtual) values for C_p of *tin* in the compound are obtained:

Temp.	C_p (tin):	Temp.	C_p (tin):
0°	5.869	900°	6.458
100	5.912	1000	6.553
200	5.961	1100	6.652
300	6.014	1200	6.757
500	6.139	1275	6.840
700	6.287	1325	6.896

These (hypothetical) values of C_p for *tin* vary with the temperature in a *quite continuous* way.

²⁾ E. COHEN and J. OLIE, Zeits. f. phys. Chem., 71, (1910), 400.

(=7.285), the agreement would be far less satisfactory: 21.64 instead of 24. From this consideration it may also be concluded, that the *tin* in *PtSn* is present in a condition, which is nearer to that of *grey*, than to that of white tin. Contrary to TAMMANN's and ROHMANN's suggestion (*loco cit.* p. 236), the heat-capacity of *PtSn* is *smaller* than the sum of those of the elements, although its specific volume is *greater* than the sum of the atomic volumes.

Further experiments of this kind now going on in this laboratory, will soon bring still stronger evidence of the fact, that the so-called "law of additive atomic heats" is certainly *not* valid for intermetallic, homopolar compounds. It is most probable then, that, *a fortiori*, it will be neither valid for *heteropolar* chemical compounds. Also this last conclusion will afterwards be tested by experiments.

*Groningen, Laboratory for Inorganic and Physical
Chemistry of the University.*

Geology. — *Migration and accumulation of oil and gas.* By J. VERSLUYS.

(Communicated at the meeting of April 2, 1932.)

Two points should be borne in mind when considering the occurrence of oil and gas in the earth's crust. Firstly, that they are encountered in the coarse sediments. Secondly, that the majority of the known oil and gas fields are situated in the highest parts of the structures, unless a fault acts as a barrier, in which case oil and gas accumulate in a coarse layer underneath it.

The problem of oil and gas concentration especially in the coarser strata was not at first considered by geologists, nor has it generally been recognized what filled the pores of the finer sediments. Without considering, properly, the reasons for the accumulation of oil and gas in the coarser sediments, the general opinion was that the coarser sediments are the only depositions which have sufficient pore space to contain oil, while the finer sediments were said to be tight. Accordingly the coarser beds, which have no exposures at the surface, are often erroneously regarded as closed reservoirs.

If it is taken for granted that oil and gas rise to the uppermost parts of the coarser strata owing to their lower specific gravity as compared to water¹⁾, and are retained there, a certain rôle is attributed to the finer grained strata, viz. that they act as barriers to the motion of oil and gas. As it has been remarked already, they were simply said to be tight. In the

¹⁾ With regard to buoyancy, the so called "shoreline pools" (XXI) and oil accumulations under planes of unconformity are under similar conditions as anticlinal fields.