sure equation for the solid given by Stull[5] and the entropies of solution calculated, the heats of solution are derived. The fact that the measured heats of solution are so close to those calculated may be taken as confirming the vapor pressure measurements.

The results may be represented by the equation

$$\log P_{\text{atm}} = -\frac{17{,}070 - \Delta\bar{H}}{4.576T} + \frac{136.60 - \Delta\bar{S}}{4.576} - 8.052 \log T$$

In selecting values of $\Delta\bar{S}$ from Fig. 3 for use with this equation, a correction should be applied for compositions between 50 and 60 mole %. It will be noted that the two points in this region, although only slightly displaced from the theoretical curve, (and that within the experimental error) are vertically as much as 0.5 cal./°C. from the line. Values in this range should therefore be corrected proportionately for the discrepancy if correct vapor pressures are to be calculated.

The phase diagram[4] shows a compound $NaAlCl_4$ to exist in the solid; the entropy measurements above suggest that it exists in the liquid also. The most reasonable assumption concerning the transfer of sodium in the gas phase is that the same compound is responsible. (Since this work was completed, Howard[6] has shown that the analogous fluoride, $NaAlF_4$, is stable in the gas phase). Owing to the lack of precision in the results given in Fig. 2 and uncertainties regarding the activities of sodium chloride in the liquid mixtures and the entropy of $NaAlCl_4$(gas) it is not possible to make precise calculations, but a ΔH of the order of −50 kcal. is indicated for the reaction

$$NaCl(gas) + AlCl_3(gas) = NaAlCl_4(gas)$$

This is unexpectedly high. In order to confirm that the transfer of sodium was in fact due to a volatile compound and not to spray or liquid films creeping over the inner surfaces of the apparatus a few additional experiments were made.

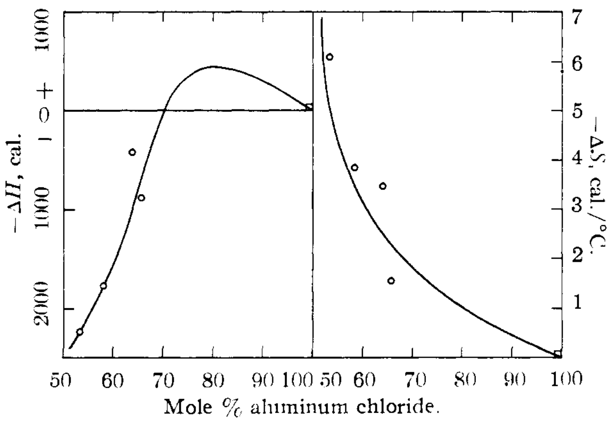

Fig. 3.—Differential heats and entropies of solution of Al_2Cl_6 in sodium chloride–aluminum chloride mixtures.

(1) Gas was passed over the liquid instead of bubbled through it—sodium was still transferred in large quantity.

(2) Some barium chloride was put in the melt—the ratio sodium:barium in the distillate was 10 times higher than in the melt.

(3) From pure liquid sodium chloride very little sodium was distilled.

(4) Distillation from one limb to the other of an inverted U-tube showed that transfer was faster in an evacuated tube than in one filled with argon at atmospheric pressure.

(5) It was shown that condensation of a liquid phase could occur at a temperature only a little below that of the liquid being distilled; this implies that the vapor was saturated.

All these results point plainly to the conclusion that distillation of sodium is by means of a volatile compound and, although there is no evidence as to its composition, the assumption that it is $NaAlCl_4$ is by far the most reasonable that can be made.

The author is deeply indebted to Dr. N. W. F. Phillips and Dr. J. P. McGeer for invaluable discussion, criticism and encouragement.

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(5) D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).

(6) E. H. Howard, THIS JOURNAL, **76**, 2041 (1954).

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INC.]

The Crystal Structures of RhTe and RhTe$_2$

BY S. GELLER

RECEIVED DECEMBER 22, 1954

The crystal structures of three rhodium tellurium phases have been determined from X-ray powder diffraction data. RhTe has the NiAs(B8) type structure. The high temperature form of $RhTe_2$ has the $Cd(OH)_2$(C6) type structure and the low temperature form has the pyrite (C2) type structure. The latter which has the lower volume per $RhTe_2$ is a superconductor at 1.51 °K. discovered by Matthias, *et al.*[1]

Introduction

Recently, Matthias reported[1] that the compound $RhTe_2$ is superconducting with a superconducting transition temperature of 1.51°K. Although not pointed out by Matthias at the time, there exist two $RhTe_2$ phases, only one of which is superconducting[2] above 1.06°K. Also there is a phase of composition RhTe which is not superconducting above 1.06°K.[2] The purpose of this paper is to report the crystal structures of the aforementioned rhodium–tellurium phases.

Apparently, Wöhler, Ewald and Krall[3] were the

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(1) B. T. Matthias, E. Corenzwit and C. E. Miller, *Phys. Rev.*, **93**, 1415 (1954).

(2) B. T. Matthias, private communication.

(3) L. Wöhler, K. Ewald and H. G. Krall, *Ber.*, **66**, 1638 (1933).

TABLE I

CRYSTALLOGRAPHIC DATA ON RHODIUM–TELLURIUM COMPOUNDS

Compound	Crystal symmetry	Systematic absences	Most probable space group	Lattice constants, Å.	Vol./unit cell, Å.[3]	X-Ray detd. density, g./cc.
RhTe	Hexagonal	(*hh·l*), *l* odd	$D_{6h}(4)$-$P6_3/mmc$	$a = 3.99 \pm 0.01$ $c = 5.66 \pm 0.01$	78.0	9.81
$RhTe_2$ (high temp. form)	Trigonal	None	$D_{3d}(3)$-$P\bar{3}m$	$a = 3.92 \pm 0.01$ $c = 5.41 \pm 0.01$	72.0	8.26
$RhTe_2$ (low temp. form)	Cubic	(0*kl*), *k* odd	$T_h(6)$-$Pa3$	$a = 6.441 \pm 0.002$	267.2	8.90

first to prepare a $RhTe_2$. The essential part of their method was the heating of $RhCl_3$ with excess Te in a CO_2 stream at about 750°. Wöhler stated that he found it impossible to obtain a more Te-rich compound than $RhTe_2$. The compound made by Wöhler, when examined under a microscope, showed fourfold symmetry.

Biltz[4] prepared a rhodium–tellurium compound in a manner similar to that of Wöhler but claimed that the true formula was Rh_2Te_5 and that this compound had a "pseudopyrite" structure.

The results of our work indicate that there are at least three phases in the rhodium–tellurium system. These are RhTe with the NiAs (B8) type[5] structure and two phases with the composition $RhTe_2$. One has the $Cd(OH)_2$(C6) type[6]; the other has the pyrite (C2) type.[7]

TABLE II

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF RhTe[a]

(*hk·l*)	*d*, Å. Obsd.	*d*, Å. Calcd.	Rel. I_0[a] [b]	Rel. I_c
10·0	3.45	3.46	w-m	27
10·1	2.94	2.95	vs	175
10·2	2.19	2.19	vs	183
11·0	1.99	1.99	s	128
10·3 20·1	1.65	1.65 1.65	m-s	61
20·2	1.47	1.47	m-s	50
00·4	1.41	1.41	w	13
20·3 21·1	1.27	1.27 1.27	m	37
21·2	1.19	1.18	m	48
11·4 30·0	1.15	1.15 1.15	m-s	62
10·5 21·3	1.07	1.07 1.07	w-m	23
22·0	0.998	0.998	w-m	16
31·1	.944	.945	w-m	14
10·6	.910	.909	w-m	17
31·2	.908	.908	m	34
30·4	.893	.893	m	34
40·1 31·3 21·5	.854	.854 .854 .855	m-s	43
20·6	.828	.827	m	24
40·2	.826	.825	m	25
22·4	.815	.815	m-s	50
10·7	.787	.787	m	18
32·1	.785	.785	m-s	38

[a] Reflections with intensity below minimum observable are omitted. [b] w = weak, m = medium, s = strong, vs = very strong.

Experimental

The compounds investigated were obtained from Matthias. The RhTe and the pyrite-type $RhTe_2$ were prepared by mixing the proper proportions of rhodium and tellurium, sealing the mixture in an evacuated fused silica tube and heating to 900° for one to three days. The $Cd(OH)_2$-type $RhTe_2$ was made in the same manner but at 1200° and quenched to room temperature.

X-Ray powder photographs were taken using CuK radiation and a Straumanis type Norelco camera with 114.6 mm. diameter. Intensities of the lines were estimated visually.

Structure Determination.—Because all of the structures reported here are well-known types, it is unnecessary to go into great detail. Pertinent crystallographic data on the compounds are given in Table I.

Relative intensities were computed using the relation

$$I = p\,|F_{hkl}|^2\,\frac{1 + \cos^2 2\theta}{\sin^2\theta\cos\theta} \times 10^{-5}$$

where p is the multiplicity and F_{hkl}, the structure amplitude. The values of the atomic scattering factors were obtained from Vol. II of the Internationale Tabellen zur Bestimmung von Kristallstrukturen. No corrections were made for absorption. In all cases the comparison of calculated with observed intensities verified the correctness of the structures. These data are shown in Tables II, III, IV.

TABLE III

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF C6-TYPE $RhTe_2$[a]

(*hk·l*)	*d*, Å. Obsd.	*d*, Å. Calcd.	Rel. I_0	Rel. I_c
00·1	5.37	5.41	w-m	34
10·1	2.87	2.87	vvs	206
00·2	2.70	2.70	vw	10
10·2	2.11	2.12	s	77
11·0	1.96	1.96	m-s	72
11·1	1.84	1.84	vw	11
20·1	1.62	1.62	w-m	35
11·2 10·3	1.59	1.59 1.59	m	44
20·2	1.437	1.439	w	21
00·4	1.352	1.353	vvw	7
21·1	1.251	1.249	w	18
20·3	1.235	1.236	vw	14
21·2	1.159	1.159	w	22
30·0	1.133	1.133	vw	12
11·4	1.114	1.114	w-m	23
21·3 30·2	1.046	1.046 1.044	w	19
10·5	1.032	1.031	vw	9
31·1	0.929	0.928	w	18
20·5	.913	.913	vw	12
31·2	.892	.890	w	17
30·4 10·6	.870	.869 .872	w-m	32
31·3	.837	.836	w	24
21·5	.828	.828	w	25
40·2	.812	.811	vw	13

[a] Reflections with intensity below minimum observable are omitted.

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(4) W. Biltz, *Z. anorg. Chem.*, **233**, 282 (1937).

(5) *Strukturbericht*, **1**, 84 (1931).

(6) *Ibid.*, **1**, 161 (1931).

(7) *Ibid.*, **1**, 150 (1931).

TABLE IV

COMPARISON OF CALCULATED WITH OBSERVED INTENSITIES OF C2-TYPE $RhTe_2$

hkl	Rel. I_0	Rel. I_c	*hkl*	Rel. I_o	Rel. I_c
111	vw	11	600	w	8
200	w	16	442		
210	vs	195	610	..	7
211	s	130	611	m	27
220	w-m	28	532		
221	..	5	620	vvw	3
311	s	135	621	vvw	5
222	w	11	540		
320	w-m	22	443		
321	s	90	541	..	1
400	vw	8	533	w-m	14
410	..	4	622	..	6
322			630	m	25
411	..	2	542		
331	..	0	631	w-m	13
420	w-m	27	444	..	2
421	m	37	632	..	2
332	w	13	543	..	2
422	w	9	711	..	1
430	..	1	551		
431	..	3	640	..	0
511	m	34	720	w-m	14
333			641		
520	m	29	721		
432			633	m	32
521	w-m	17	552		
440	m	33	642	w-m	17
522	..	3	722	..	3
441			544		
433	..	1	731	m-s	84
531	vvw	3	553		

In the case of RhTe, all atoms are in special positions of space group $D_{6h}(4)$-$P6_3/mmc$

2Rh in 2(a): 000; 00 $^1/_2$
2Te in 2(c): $^1/_3$ $^2/_3$ $^1/_4$; $^2/_3$ $^1/_3$ $^3/_4$

In the case of the high temperature modification of $RhTe_2$ ($Cd(OH)_2$ type), a single crystal was isolated and Weissenberg and Buerger precession photographs taken. The diffraction symmetry of these photographs is D_{3d}-$\bar{3}m$. As there are no systematic absences, the most probable space group was easily established to be $D_{3d}(3)$-$P\bar{3}m$. In the $RhTe_2$ structure the atoms are in the following special positions

1Rh in 1(a): 000
2Te in 2(d): $^1/_3$ $^2/_3$ z; $^2/_3$ $^1/_3$ $\bar{z}$

The single parameter z_{Te} was taken to be 0.25 in the calculation of intensities. This value is probably correct to within ±0.005.

Finally, in the case of the low temperature modification of $RhTe_2$, the Rh atoms occupy 4(a), (000; 0 $^1/_2$ $^1/_2$; ↻) and the Te atoms 8(c), $\pm$ (xxx; $^1/_2 + x$, $^1/_2 - x$, $\bar{x}$; ↻) of space group $T_h(6)$-$Pa(3)$. The value of the single Te parameter was deduced from a comparison with the $RhSe_2$[8] structure in which the parameter was determined very accurately from quantitative intensity measurements. In this structure, the distance of closest approach between two Se atoms, 2.50 Å., is somewhat larger than the elementary Se–Se distance, 2.32 Å. The Te parameter in $RhTe_2$ was therefore deduced by multiplying the elementary Te–Te distance 2.86 Å. by the obvious ratio leading to a probable Te–Te distance in the crystal of 3.08 Å. and to $x_{Te} = 0.362$. This value leads to very good agreement (see Table IV) between calculated and observed intensities and is felt to be accurate within ±0.005.

Discussion

The interatomic distances and numbers of equivalent neighbors are shown in Tables V, VI, VII.

TABLE V

INTERATOMIC DISTANCES IN RhTe

Atom	No. of equiv. neighbors	Neighboring atom	Distance, Å.
Rh	6	Te	2.70
Rh	2	Rh	2.83
Rh	6	Rh	3.99
Te	6	Rh	2.70
Te	6	Te	3.99
Te	6	Te	3.65

TABLE VI

INTERATOMIC DISTANCES IN $RhTe_2$ (C6-TYPE)

Atom	No. of equiv. neighbors[a]	Neighboring atom	Distance, Å.
Rh	6	Te	2.64
Rh	6	Te	4.65
Rh	6	Rh	3.92
Te	3	Rh	2.64
Te	6	Te	3.92
Te	6	Te	3.52
Te	3	Rh	4.65

[a] Under the assumption that z_{Te} is exactly equal to $^1/_4$.

TABLE VII

INTERATOMIC DISTANCES IN $RhTe_2$ (C_2-TYPE)

Atom	No. of equiv. neighbors	Neighboring atom	Distance, Å.
Rh	6	Te	2.65
Rh	6	Te	4.30
Rh	2	Te	4.04
Rh	12	Rh	4.55
Te	1	Te	3.07
Te	3	Rh	2.65
Te	3	Te	3.53
Te	3	Te	3.95
Te	3	Rh	4.30
Te	1	Rh	4.04

No melts with compositions between RhTe and $RhTe_2$ were photographed so that it is not known whether the transformation from the B8 to the C6 structure is similar to the continuous transformation of CoTe to $CoTe_2$.[9] It is quite probable that it is. But the transition of $RhTe_2$ from the high temperature to the low temperature form is unlike that of $CoTe_2$. In the latter case, the low temperature phase has the marcasite (C18) type structure.[10]

The transition from the C6 to the C2 type probably does not affect significantly the valence of the Rh atom. In both structures the six nearest neighbors to an Rh atom are Te atoms at the distance 2.64 Å. The other atoms surrounding the Rh are in both cases so far from the Rh atom as to have no real effect on its valence. The Te–Rh–Te angles are 96° in the C6-type and 84° in the C2 type. The surroundings of a Te atom in the two structures are quite different, however. In particular, the Te–Te atoms occur in pairs, which may be said to be Te–Te molecules, the distance between atoms in these pairs, 3.07 Å., being somewhat larger than the elemental Te diameter,

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(8) S. Geller and B. B. Cetlin, to be published.

(9) S. Tengner, *Z. anorg. allgem. Chem.*, **239**, 126 (1938).

(10) *Strukturbericht*, **1**, 495 (1931).

2.86 Å. There does appear to be a valence change in Te involved in the transition.

The transition from C6 to C2 type is not a simple one. Examination of the structures leads one to the conclusion that the transition probably involves a displacement in the (11·1) planes as well as motion perpendicular to these planes. The transition also involves an appreciable contraction. The phase with the higher density (C2) is the one which is superconducting at 1.51°K.

The C6-type $RhTe_2$ appears in metallically lustrous plates with the trigonal axis perpendicular to the plate.

It is known that a substance must be a metal at room temperature in order to be a superconductor at a lower temperature. It has also been shown that a decrease in volume tends to decrease the superconducting transition temperature particularly in the case of elements (see D. Shoenberg[11]). Measurements of resistivity of the C6 type $RhTe_2$ (containing an excess of Te) were made by Dr. T. H. Geballe who found a value of 0.0035 ohm-cm. at room temperature 0.0030 ohm-cm. at 78°K. and 0.0015–0.0020 ohm-cm. at 20°K., indicating that this phase is either metallic or a degenerate semiconductor.

Hardy and Hulm[12] have reported the only case in which two intermetallic phases with the same composition are both superconducting. These are the thorium silicides $(ThSi)_2$. However, no crystallographic data are as yet available on one of these phases.

Acknowledgments.—The author wishes to thank Dr. B. T. Matthias for initiating this problem, Dr. T. H. Geballe for making the resistivity measurements, Dr. H. W. Lewis for helpful discussions. The excellent work performed by Mr. R. Goldstein in measuring the powder photographs and calculating the intensities and by Mr. E. Corenzwit in taking the powder photographs is gratefully acknowledged.

MURRAY HILL, N. J.

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[11] D. Shoenberg, "Superconductivity," Cambridge University Press, London, 1952.

[12] G. F. Hardy and J. K. Hulm, *Phys. Rev.*, **93**, 1004 (1954).

NOTES

On the Binding Energies of Some Molecular Compounds between *p*-Benzoquinone and Various Aromatic Substances

BY AKIRA KUBOYAMA[1] AND SABURO NAGAKURA

RECEIVED DECEMBER 20, 1954

In order to investigate the mechanism of the molecular compound, measurements of binding energies and characteristic absorption spectra seem to be very important.[2] Then we have measured spectrophotometrically these two quantities with molecular compounds between *p*-benzoquinone (electron acceptor by the Mulliken's definition[3]) and various aromatic substances (electron donor), such as phenol, anisole, hydroquinone, hydroquinone dimethyl ether, benzene, toluene, *o*-, *p*-xylene, naphthalene, phenanthrene and anthracene. These measurements are made with ternary solutions containing small amounts of electron acceptor and donor in a solvent. The results are given in Tables I and II. In Table I, values of the corresponding binding energy obtained by other authors, if any exist, are also shown for the purpose of comparison.

TABLE I

THE BINDING ENERGIES ($-\Delta H$) OF VARIOUS QUINHYDRONE TYPE MOLECULAR COMPOUNDS

Electron donor	Solvent	$-\Delta H$ (kcal./mole)	$-\Delta H'$[a] (kcal./mole)
Hydroquinone	Water (0.06 mole HCl)	2.9 ± 0.1	2.4 ± 0.4[b]
Hydroquinone	Water (0.05 mole HCl)		5.2 ± .4[c]
Dimethyl ether	*n*-Heptane	1.8 ± .1	3.5 ± .7[c]
Dimethyl ether	Carbon tetrachloride	2.1 ± .2	
Phenol	*n*-Heptane	6.6 ± .4	4.8 ± .3[c]
Phenol	Water (0.06 mole HCl)	1.2 ± .2	
Phenol	Carbon tetrachloride	4.3 ± .2	
Anisole	*n*-Heptane	1.3 ± .1	
Anisole	Carbon tetrachloride	1.2 ± .1	

[a] $-\Delta H'$ denotes the values obtained by other authors. [b] A. Berthold and S. Kunz, *Helv. Chim. Acta*, 21, 17 (1938). This value was obtained by the solubility measurement. [c] H. Tsubomura, *Bull. Chim. Soc. Japan*, 26, 304 (1953). These values were obtained by the spectroscopic method.

TABLE II

THE BINDING ENERGIES AND THE POSITIONS OF THE CHARACTERISTIC ABSORPTION BANDS OF MOLECULAR COMPOUNDS BETWEEN SEVERAL AROMATIC HYDROCARBONS AND *p*-BENZOQUINONE

Electron donor	Solvent	$-\Delta H$ (kcal./mole)	λ (mμ)	I.P. (e.v.)
Benzene	*n*-Heptane	1.8 ± 0.4	305(20°)	9.24[a]
Toluene	*n*-Heptane	1.8 ± .3	315(20°)	8.82[b]
o-Xylene	*n*-Heptane	1.8 ± .4	322(20°)	8.58[b]
p-Xylene	*n*-Heptane	1.7 ± .3	320(15°)	8.48[b]
Naphthalene	*n*-Heptane	1.5 ± .3	360(15°)	8.1[b]
Naphthalene	Carbon tetrachloride	1.4 ± .3	373(15°)	
Phenanthrene	Carbon tetrachloride	1.8 ± .4	380(15°)	
Anthracene	Carbon tetrachloride		450(7°)	

[a] W. C. Price and R. W. Wood, *J. Chem. Phys.*, **3**, 439 (1935). [b] V. G. Hammond, W. C. Price, J. P. Teegan and A. D. Walsh, *Discs. Faraday Soc.*, **9**, 53 (1950).

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[1] Present address is the Department of Agriculture, Miyazaki University.

[2] Until now, many spectrophotometric investigations have been made with organic molecular compounds involving *p*-benzoquinone and its derivatives as electron acceptor: L. Michaelis and S. Granick, THIS JOURNAL, **66**, 1023 (1944); H. Tsubomura, *Bull. Chem. Soc. Japan*, **26**, 304 (1953); G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **58**, 249 (1954).

[3] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).