Elektronegativitäten zu bestimmen. Beide Verfahren benutzen als Ausgangspunkt die Bildungswärmen. Bei der hier entwickelten Methode wird jedoch als neues Element der Atomabstand mit berücksichtigt, was eine direkte Bestimmung der effektiven Atomladungen ermöglicht.

Herrn Dr. H. KIMMEL danke ich für zahlreiche wertvolle Diskussionen.

Thermoelectric Power of Silver Iodide

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The thermal emf of silver iodide has been measured between 190 and 510 °C using silver electrodes. The results can be described by the following equation[1]:

$$-\varepsilon = 0.722 \pm 0.001 - (0.407 \pm 0.014) \cdot 10^{-3} \cdot T_m ,$$

ε is the SEEBECK coefficient in mV $^\circ C^{-1}$ and T_m is the mean temperature of the salt column. The results are compared with earlier measurements.

The cubic modification of silver iodide[2], which is stable between the transition point 147 °C and the melting or decomposition point 555 °C, is characterized by the high mobility of the cations. WEISS[3] has measured the electrical conductance of this α-modification, and he found an increase in electrical conductivity with increasing iodine pressure. From this investigation and from measurements of the thermal emf in N_2 atmosphere WEISS[4] has concluded that the cause of these anomalies is the formation of electron holes according to:

$$\tfrac{1}{2}\, I_2(\text{gas}) = I^- + \oplus \, .$$

Under iodine pressure α-AgI absorbs measurable quantities of I_2 (l. c.[5]), and therefore the possibility cannot be excluded that the increase in conductivity is caused by an increase in the mobility of the cations.

The temperature dependence of the thermal emf should also show anomalies, if the conductivity measurements and theories by WEISS are correct.

The following equation is valid for a galvanic cell, according to REINHOLD[6]:

$$\varepsilon = \varepsilon_2 - \varepsilon_1 \, ,$$

ε is the temperature coefficient of the emf of the isothermal system $Me/MeX/X_2$, ε_2 and ε_1 are the thermal emf's of the systems $X_2/MeX/X_2$ and $Me/MeX/Me$ respectively.

The coefficient ε can also be determined from thermodynamic properties:

$$E = -\frac{1}{F} \cdot \Delta G \, ,$$

$$\varepsilon = \frac{dE}{dT} = -\frac{1}{F}\frac{d\,\Delta G}{dT} = \frac{1}{F}\,\Delta S ;$$

F = FARADAY's constant, ΔS = the entropy change, ΔG = the change of GIBBS' free energy.

Experimental

Reagent grade salt (B. D. H. or Hopkin & Williams) was used without further purification. The experiments were performed both in air and argon atmosphere, but no differences in the results could be detected.

Salt slabs, about 20 mm high and 10 mm in diameter were made in a small hand press. A slab was placed between two silver electrodes, connected to the potentiometer bridge with silver leads. In the first series of experiments, the electrodes were silver discs, 0.8 mm thick and 10 mm in diameter. Chromel-alumel thermocouples were soldered to the back of the electrodes. The temperatures measured were corrected for the temperature differences across the thickness of the silver discs. To minimize the errors of the temperature measurements some experiments were performed with electrodes made of silver foils, which were folded; and the thermocouples were stuck in between. In this case the small temperature gradients in the electrodes could be neglected. The salt disc with electrodes was placed be-

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[1] All stated errors in this paper are standard deviations.

[2] G. BURLEY, American Mineralogist **48**, 1266 [1963].

[2] K. WEISS, Dissertation, Göttingen 1956.

[4] K. WEISS, Z. Phys. Chem., N.F. **32**, 256 [1962].

[5] K. WAGENER, Z. Phys. Chem., N.F. **25**, 135 [1960].

[6] H. REINHOLD, Z. Elektrochem. **39**, 290 [1933].

tween two steel plates in a furnace. The plates could be heated separately and were electrically insulated from the electrodes by thin sheets of mica.

Both the temperature difference between the electrodes and the mean temperature of the salt slab were varied. The first experiments were performed with a temperature differene (ΔT) of about 10 °C, but since it was found that the temperature dependence of the emf was linear, ΔT was increased to about 30 °C. The emf was strictly proportional to ΔT, cf however Weiss[4]. The interval between two measurements was about one hour, which was the time required for the temperature to become stable. No time dependence of the emf could be observed with these reversible electrodes[7].

All voltages were measured with a Croydon DC potentiometer, using a galvanometer as a null detector.

Discussion

The thermal emf of silver iodide has been investigated by several authors.

Reinhold[8] measured the emf (ε_1) of α-AgI with silver electrodes and he gave the value

$$\varepsilon_1 = -0.56 \text{ mV/°C} .$$

He did not find any dependence on the mean temperature.

The results obtained by Weiss[4] show a large straggling, which he assumed to be due to differences in the chosen ΔT. The dependence on the mean temperature was claimed to be irregular.

In our measurements we have found that ε_1 of α-AgI depends on the mean temperature (Fig. 1) and that it can be described by the following linear relation

$$-\varepsilon_1 = 0.722 \pm 0.001 - (0.407 \pm 0.014) \cdot 10^{-3} \cdot T_m \quad \text{mV/°C},$$

T_m is the mean temperature in °C.

The slope of the line is negative, which is the most common case for solid ionic salts[7].

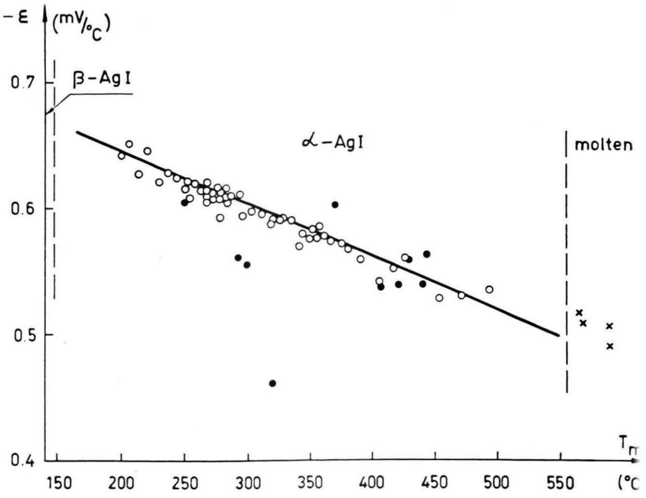

Fig. 1. Dependence of the thermal emf of Ag/AgI/Ag on the mean temperature. ○: present experiments; ●: according to Reinhold[8]; ×: according to Markov[9].

Markov[9] has measured the thermal emf of molten AgI and it seems as if there is no marked change in the emf at the melting point.

The thermal emf (ε_2) of the system I_2/AgI/I_2 has recently been measured by Wagener[10] and his results have been used in Table 1, column III. $\varepsilon_2 - \varepsilon_1$ and $\Delta S/F$ coincide within the limits set by the experimental errors (Table 1). As $\Delta S/F$ was calculated under the assumption that α-AgI is a pure ionic conductor the thermal emf-measurements do not support the assumption that the increase of the electrical conductivity observed by Weiss is caused by electron holes.

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I T_m °C	II $-\varepsilon_1$ Ag/AgI/Ag mV/°C	III $-\varepsilon_2$ I_2/AgI/I_2 mV/°C	IV $-\varepsilon_{exp} = \varepsilon_1 - \varepsilon_2$ Ag/AgI/I_2 mV/°C	V $-\varepsilon_{cal} = -\Delta S/F$ mV/°C	VI $\varepsilon_{exp} - \varepsilon_{cal}$ mV/°C
150	0.661	1.14	0.479	0.410	−0.069
200	0.641	1.08	0.439	0.396	−0.043
250	0.620	1.03	0.410	0.386	−0.024
300	0.600	0.99	0.390	0.374	−0.016
350	0.578	0.95	0.372	0.364	−0.008
400	0.559	0.91	0.351	0.354	+0.003
450	0.539	0.87	0.331	0.345	+0.014

Table 1. Comparison of ε as estimated from the measurements with ε calculated from thermodynamic properties.

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[9] B. F. Markov, Dokl. Akad. Nauk, SSSR **108**, 115 [1956].

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