THERMAL EXPANSION OF SODIUM AND POTASSIUM CHLORIDES FROM LIQUID-AIR TEMPERATURES TO +300° C.

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ABSTRACT

The thermal expansion coefficients of sodium and potassium chloride were measured from liquid-air temperatures to +300° C. The expansion coefficients of iron pyrites from liquid-air temperature to 0° C., and of rock-salt from room temperature to 300° C. are also reported.

The Gruneisen constants for NaCl and KCl are shown to decrease with temperature. In potassium chloride the decrease is more rapid.

A comparison of the lattice expansion coefficients and the macroscopic expansion coefficients of sodium and potassium chlorides has been made. The need for an accurate lattice expansion measurement of sodium chloride at high temperatures is emphasised. In potassium chloride a systematic difference exists between the values of the author and the lattice expansion values of Glover. Though the experiments have been carried out on different specimens this difference is small and is just on the limit of experimental error.

Also it is shown that rock-salt and sodium chloride possess identical expansion coefficients within the limits of experimental error.

1. INTRODUCTION

The measurement of thermal expansion at low temperatures is of great importance to the theory of the solid state. Yet such measurements are present only for very few crystals. In any theory of the solid state, the alkali halides occupy an important position since the forces of binding in the crystal lattice are known without any ambiguity for them. It is surprising to find that except in the case of sodium chloride, no experiments on the variation of thermal expansion with temperature at low temperatures are present for the other alkali halides. Experiments have been undertaken by the author to fill this gap and the results of measurements on potassium chloride are reported in this paper. The results on potassium bromide and potassium iodide will follow. The low temperature expansion of iron pyrites and sodium chloride are also reported as they serve as a check on the accuracy of measurement. Their low temperature expansion values are present in the literature.

The macroscopic expansion of KCl above room temperatures has been investigated by Eucken and Dannohl. But their results appear to suffer from a systematic error. So the macroscopic expansion of potassium chloride has also been measured up to 300° C.

2. PREVIOUS WORK

The thermal expansion of potassium chloride has been measured by the interferometric technique by Fizeau (1867) at 40° C. Klemm, Tilk and Mullenheim (1928), employing a pyknometer method, determined the expansion coefficient of potassium chloride at 60° and 135° C. Their value is in good agreement with that of Fizeau. The only measurement over an extended temperature range was made by Eucken and Dannohl (1934) using their novel heterodyne beat method. Unfortunately their value at room temperature is much smaller than those of the abovementioned authors. The mean volume expansion coefficient between −79° to 0° C., and −184° to −79° C. was measured by Henglein (1925) employing a gas volumenometer.

The lattice expansion of potassium chloride was investigated by Kantola (quoted in Glover, 1954) at a mean temperature of 61° C. His value is in good agreement with Fizeau's macroscopic measurement. Vegard (Glover. 1954) has also measured the lattice expansion at a mean temperature of 164° C.; but his value is too low and the experimental accuracy is not stated. The lattice expansion up to 600° C. has recently been measured by Glover (1954) with a precision X-ray method. He employed pure and calcium-containing potassium chloride specimens and found that with the impurity contents employed by him, he could detect no change in the lattice constants in different specimens. He derived the true expansion coefficient from his measurements and found it to vary linearly with temperature.

The macroscopic expansion coefficient of sodium chloride at 40° C. was measured by Fizeau (1867). The expansion coefficient of sodium chloride at high temperatures has been determined by Eucken and Dannohl (1934) and Walther *et al.* (1937). The expansion of sodium chloride down to liquid-air temperatures has been investigated by Buffington and Latimer (1936). The mean volume expansion coefficient between −184/−79° C. and −79/0° C. has been measured by Henglein (1925). The lattice expansion of sodium chloride has been measured by Geiss (1924), James (1925), Saini (1934), Straumanis and Ievins (1936), and Basu and Maitra (1938). The lattice expansion of sodium chloride between −253/−193° C. has been determined by Lindemann (1912).

The expansion of iron pyrites at room temperatures was measured by Fizeau (1868). The high temperature expansion of iron pyrites has been investigated by Press (1949) and Sharma (1951). The expansion of pyrites down to liquid-air temperatures was measured by Valentiner and Wallott (1915).

3. EXPERIMENTAL ARRANGEMENT

The high temperature apparatus set up by Press (1949) and the low temperature apparatus set up by Sridhar (1952) have been used for this purpose. The potentiometer assembly and the method of measurement have already been described in a previous paper by the author (1955). Only a brief mention will be made about the method of calibration of the copper constantan thermocouple used for low temperature measurements.

There were no standard thermometers with which the thermocouple could be calibrated. Hence the calibration was carried out according to the procedure described by Scott (1941). The thermo E.M.F. at the sublimation point of carbon dioxide is measured. The thermocouple is immersed in a Dewar flask containing crushed solid carbon dioxide. A small heater at the bottom of the Dewar flask causes the carbon dioxide to sublimate and the gas issues in a continuous stream. If this precaution is not taken, the thermocouple reads a lower temperature as the carbon dioxide is no longer in equilibrium with its own vapour. As soon as the heater is switched on the thermocouple indicates a rise in temperature and after a few minutes assumes a steady value. The measured thermo E.M.F. was 2761 μv. The temperature of solid carbon dioxide in equilibrium with its vapour at a pressure of 648 mm. mercury is calculated from the following equation given in *International Critical Tables*:

$$\mathrm{T}^\circ\,\mathrm{C.} = -\,78\cdot51 + 0\cdot0159\,(p - 760) - 0\cdot000011\,(p - 760)^2$$

and comes out to be $-80\cdot43^\circ$ C.; and the corresponding thermo E.M.F. for a standard copper constantan thermocouple from the *International Critical Tables* is 2778 μv. The deviation of $-17\,\mu v$ is plotted against the observed E.M.F. and a straight line is drawn joining the origin and this point. The deviation at any other temperature can be read off. This linear relation was found for many of the copper-constantan thermocouples sent to the National Bureau of Standards for calibration; and Scott is of the opinion that by such a calibration an accuracy of $\pm 2\,\mu v$ can be obtained.

4. RESULTS

In Tables I–III the thermal expansion coefficients of pyrites and sodium and potassium chlorides are given. Curves for the variation of expansion coefficients of sodium and potassium chlorides are given in Figs. 1 and 2. In the tables are also given the macroscopic expansion values determined by other authors. A comparison with the lattice expansion coefficients found in the literature will be made elsewhere.

TABLE I

Thermal Expansion of Iron Pyrites

T° C.	$\alpha \times 10^6$ (author)	$\alpha \times 10^6$ (Valentiner and Wallott, 1915)
−102	5·16	5·39
− 85	6·11	6·03
− 70	6·61	6·57
− 57	6·75	6·98
− 44	7·53	7·37
− 28	7·81	7·82

TABLE II

Thermal Expansion of Pure Sodium Chloride and Rock-Salt

T° C.	$\alpha \times 10^6$ (author)		Value in literature, author and year		
	Pure sod. chloride	Rock-salt			
−133·0	29·7		30·9		Buffington and Latimer (1926)
−121·0	31·7		32·1		
−109·8	33·8		33·2		
− 88·0	35·1		34·7		
− 67·2	35·9		35·8		
− 46·5	36·8		36·8		
− 26·8	37·9		37·7		
− 9·3	39·6		38·5		
+ 13·9	40·2		39·3		
			Mean value of $\alpha \times 10^6$	ΔT° C.	Author
			36·7	− 79/0	Henglein (1925)
			31·0	−184/−79	
			T° C.	$\alpha \times 10^6$	
42	40·3	42·1			Author
80	41·3	43·2	0	40·3	Eucken and Dannohl (1934)
117	43·4	44·8	100	41·3	
152	44·7	45·7	200	43·6	
183	46·6	47·6	300	47·2	
216	47·6	48·4	0	39·0	Walther *et al.* (1937)
248	49·5	49·2	100	41·9	
277	50·6	50·0	300	47·2	
			40	40·4	Fizeau (1867)

TABLE III

Thermal Expansion Coefficient of Potassium Chloride

T° C.	$\alpha \times 10^6$ (author)	Value in literature, author and year			
		Mean expansion coefficient $\alpha \times 10^6$ (Henglein, 1925)	ΔT° C.	Mean temp. T° C.	Value of present author
−164·0	22·0				
−141·4	25·9				
−122·5	29·3				
−109·5	30·6				
− 92·0	32·6	29·9	−184/−79	−132	28·0
− 75·6	33·5	33·7	− 79/0	− 39·5	34·4
− 61·0	34·2	36·7	0/50	25	36·8
− 30·2	34·5				
		T° C.	$\alpha \times 10^6$	Author	Present value of $\alpha \times 10^6$
0	35·2				
15·0	35·9				
56·3	38·0	40	38·0	Fizeau (1867)	37·6
91·0	39·3	60	37·7 ± 0·8	Klemm *et al.* (1928)	38·0
123·6	40·2				
156·7	41·0	135	39·7 ± 0·8	,,	41·2
188·5	42·6	0	31·9	Eucken and Dannohl (1934)	35·2
220·7	45·1	100	35·4		39·8
249·9	46·4	200	39·3		44·0
277·6	47·8	300	43·6		47·6

5. DISCUSSION

Two important points emerge from a study of the abovementioned tables:

1. The agreement between the author's values for the low temperature expansion coefficient of pyrites and sodium chloride with the values in the literature thoroughly justifies the method used in calibrating the copper-constantan thermocouple. The agreement is all the more gratifying when it is remembered that the experiments on pyrites and sodium chloride were performed by two entirely separate investigators.

2. Comparing the high temperature expansion coefficients for KCl with the values in literature we note that the agreement between the author's values and those of Fizeau and Klemm *et al.* is very good; but Eucken and Dannohl's values are too low. This definitely points to some systematic error in their measurements. It might be mentioned here that their values for potassium iodide do show such a disagreement with the macroscopic and X-ray values of Gott (1942), and Connell and Martin (1951) and with the values determined by the present author (to be published).

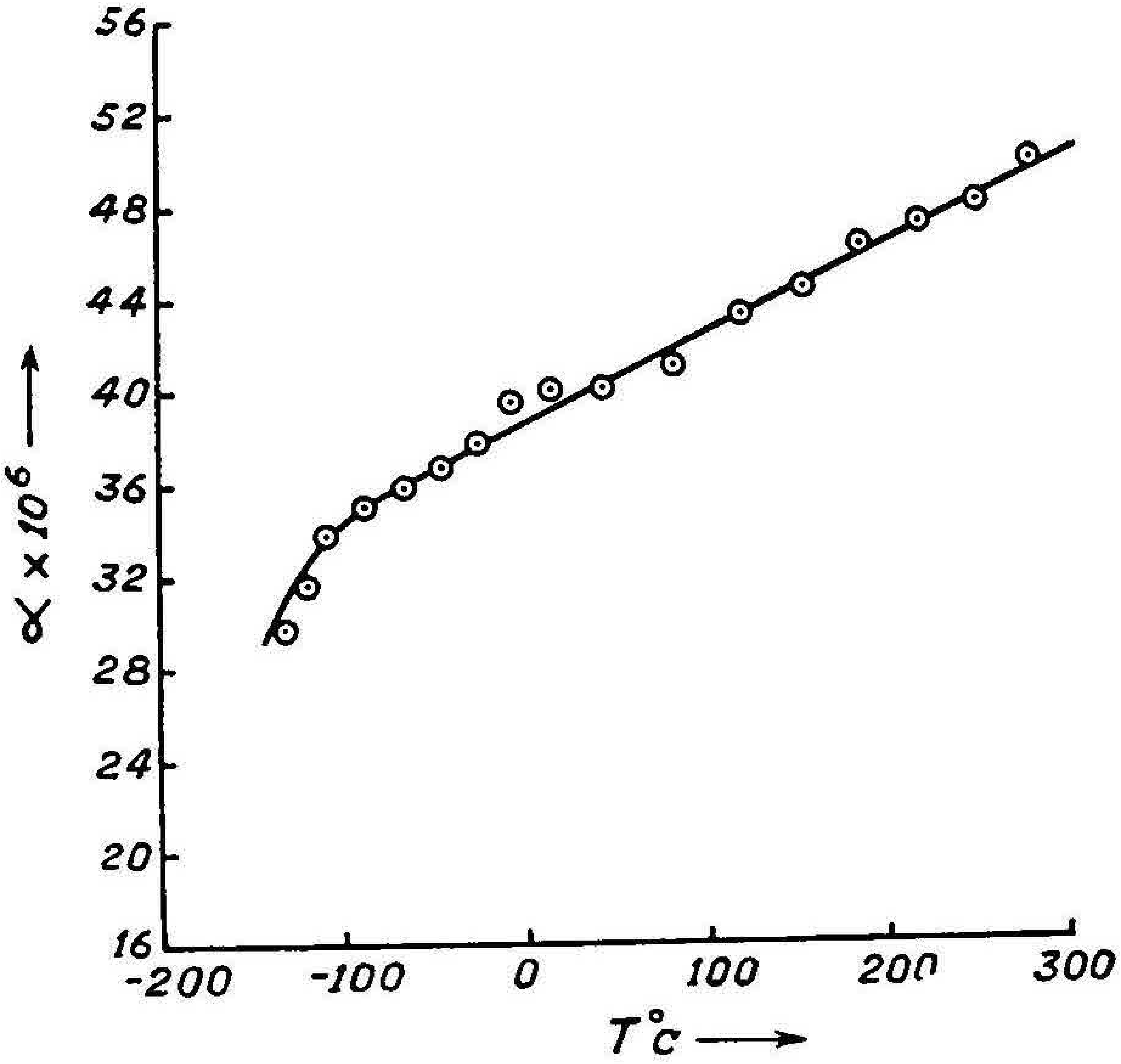

FIG. 1. α.*vs*.T curve for NaCl.

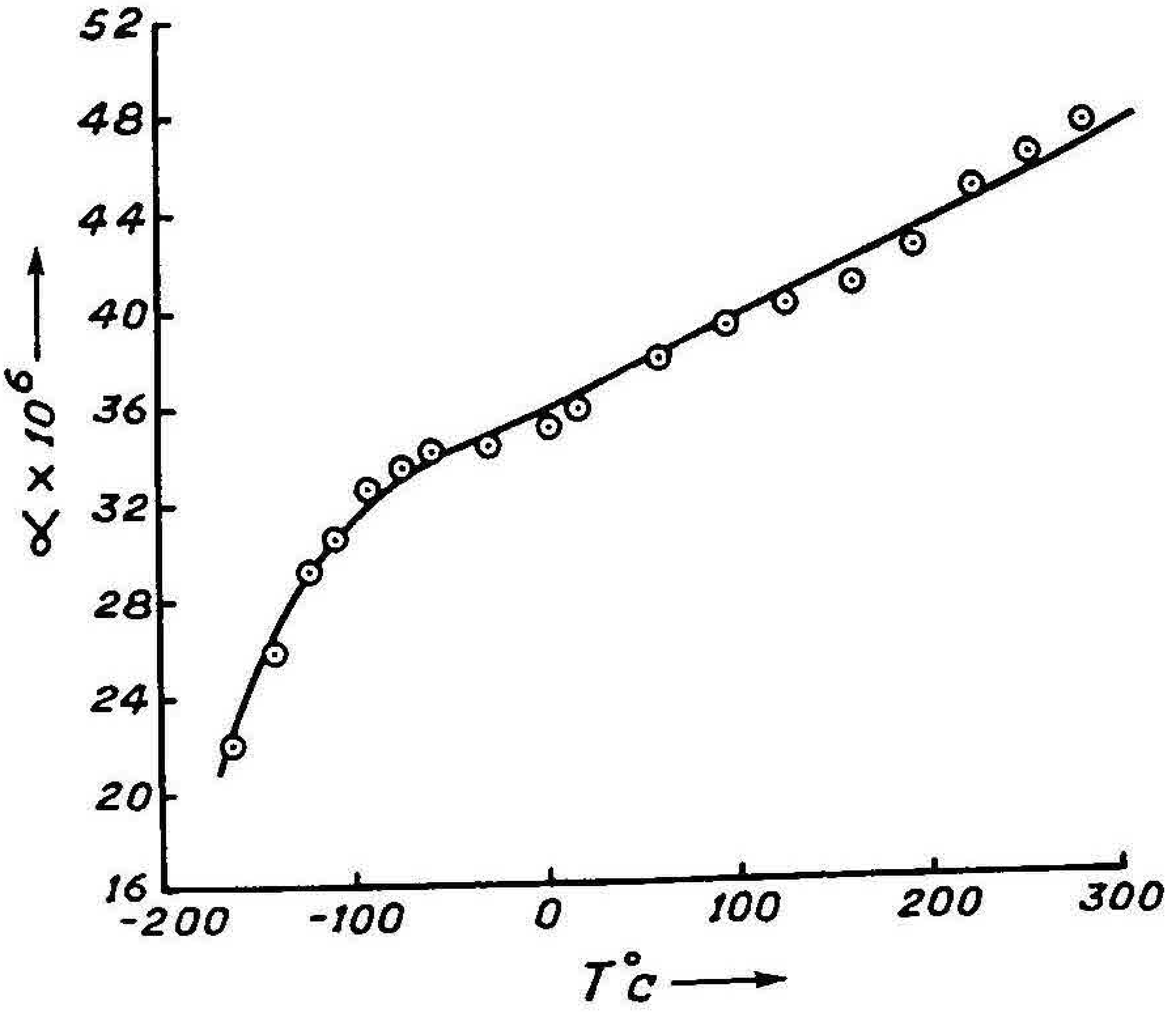

FIG. 2. α.*vs*.T curve for KCl.

It will be of interest to calculate the Gruneisen constant for sodium and potassium chlorides and to see how it varies as the temperature is reduced. The specific heat of sodium and potassium chlorides have been taken from a paper by C. S. Venkateswaran (1941), who has given the molar specific heats at constant volume for both these substances. The specific heat at constant volume has been derived by him from the observed specific heats by applying the following corrections:

$$C_p - C_V = 2\cdot7\, C_p{}^2 \times T \times 10^{-5} \text{ cals./gm. atom for NaCl}$$

and

$$C_p - C_V = 2\, C_p{}^2 \times T \times 10^{-5} \text{ cals./gm. atom for KCl}$$

The molar volume V for the two chlorides have been taken from Henglein's paper (1925). The compressibility at absolute zero for sodium and potassium chloride has been found by Durand (1936) from an extrapolation of his data of the compressibilities at 80° K. The Gruneisen constants calculated thus are given in Table IV.

TABLE IV

The Gruneisen Constants for Sodium and Potassium Chlorides down to Liquid-Air Temperatures

NaCl: Molar volume $V_0 = 26\cdot4$ c.c.; Compressibility $K_0 = 3\cdot7 \times 10^{-12}$ -- cm.^{2}/dyne

KCl: Molar volume $V_0 = 36\cdot7$ c.c.; Compressibility $K_0 = 4\cdot8 \times 10^{-12}$ -- cm.^{2}/dyne

Sodium chloride				Potassium chloride			
T° C.	Volume expansion coefficient $\beta \times 10^6$	Molar specific heat C_v cals./gm.mol.	Gruneisen constant γ	T° C.	Volume expansion coefficient $\beta \times 10^6$	Molar specific heat C_v cals./gm.mol.	Gruneisen constant γ
−173	76	8·28	1·57	−152	72·0	10·04	1·31
−153	85	9·08	1·60	−132	83·0	10·60	1·43
−133	92	9·64	1·63	−110	92·0	10·96	1·53
−113	99	10·05	1·68	− 93	96·0	11·13	1·58
− 93	103	10·38	1·69	− 72	100·0	11·32	1·61
− 73	107	10·67	1·71	− 32	104·0	11·58	1·64
− 38	112	11·10	1·72	+ 12	109·0	11·72	1·70
+ 27	119	11·60	1·75				

We find from this table that the Gruneisen constants for both sodium and potassium chlorides decrease with temperature. In potassium chloride the decrease in Gruneisen constant is more rapid.

We will now compare the macroscopic expansion coefficients of sodium and potassium chlorides with the lattice expansion coefficients present in the literature. In Table V are given the macroscopic expansion coefficients of the author and the lattice expansion coefficients found in the literature for sodium chloride and rocksalt. In Table VI these values are collected for potassium chloride.

TABLE V

Lattice and Macroscopic Expansion Coefficients of Pure Sodium Chloride and Rock-Salt

T° C.	Lattice expansion coefficient $\alpha\times10^6$ for pure NaCl	Lattice expansion coefficient $\alpha\times10^6$ for rock-salt	Author	Macroscopic expansion coefficient $\alpha\times10^6$ for pure NaCl	Macroscopic expansion coefficient $\alpha\times10^6$ for rock-salt
50	40·9	..	Lindemann (1912)	41·2	..
Not stated	40·5	..	Geiss (1924)	..	..
0–500	38·3	..	James (1925)	..	..
0	35·5	35·8	Saini (1934)	39·2	40·7
50	40·0	39·8		41·2	42·4
100	44·4	43·8		43·1	44·0
140	48·0	47·0		44·7	45·3
140–220	47·0	44·5		46·2	46·6
18– 67	40·5	..	Straumains and Ievins (1936)	40·9	42·1
18–130	..	38·08	Basu and Maitra (1938)	..	43·1
18–182	..	39·01		..	44·0
18–196	..	39·93		..	44·2
18–250	..	41·35		..	45·1
18–300	..	41·58		..	45·9
18–450	..	41·97		..	48·4

TABLE VI

Lattice and Macroscopic Expansion Coefficients of Potassium Chloride

T° C.	Lattice expansion coefficient $\alpha\times10^6$ for KCl	Author	Macroscopic expansion coefficient $\alpha\times10^6$ for KCl
25–97	38·0	Kantola	38·4
18–310	36·0	Vegard	42·4
0	34·6	Glover (1954)	36·0
50	36·4		38·0
100	38·1		39·9
150	39·9		41·9
200	41·7		43·8
250	43·5		45·8
300	45·3		47·7

The macroscopic expansion coefficients of sodium chloride, rock-salt and potassium chloride can be represented by the following equations:

$$\alpha_{\mathrm{NaCl}} = 39\cdot2\times10^{-6} + 3\cdot9\times10^{-8}\,t^\circ\,\mathrm{C}.$$
$$\alpha_{\text{rock-salt}} = 40\cdot7\times10^{-6} + 3\cdot3\times10^{-8}\,t^\circ\,\mathrm{C}.$$
$$\alpha_{\mathrm{KCl}} = 36\cdot0\times10^{-6} + 3\cdot9\times10^{-8}\,t^\circ\,\mathrm{C}.$$

From a study of the above tables we note the following points:

In the case of sodium chloride, the agreement between the macroscopic expansion coefficient and lattice expansion coefficient at 50° C. is very good in spite of the fact that different investigators employed different specimens. The only experiment on pure sodium chloride to determine the variation of expansion coefficient with temperature was carried out by Saini (1934) with a powder photograph method. He claims an accuracy of $\pm1\%$. He detected a rapid change in the expansion of sodium chloride up to 140° C. Between 140 to 220° C. he found the expansion coefficient to remain a constant. A comparison of his values with the macroscopic expansion of sodium chloride shows a fair degree of agreement. It should be emphasized that a determination of the lattice expansion of sodium chloride up to the highest temperatures, with a precision method as that of Glover (1954) would be of great value as it might serve to find out whether the lattice and macroscopic expansion coefficients agree between themselves till the highest temperatures or not.

Basu and Maitra (1938) employed the Bragg method to measure the expansion of a single crystal of rock-salt up to 450° C. They found very little change in the expansion coefficient of rock-salt. In fact they assert that the true expansion coefficient $\alpha = \frac{1}{l_t}, \frac{dl}{dt}$ for rock-salt remains constant over the range of temperatures of 18 to 450° C. In view of the fact that the macroscopic expansion coefficient shows a considerable increase over the same temperature range, Basu and Maitra's findings appear strange.

The lattice expansion coefficient of potassium chloride has been measured by Kantola, Vegard and Glover (1954). The results of the first two experimenters are quoted in Glover's paper. The macroscopic expansion coefficient value of the author and the lattice expansion coefficient value of Kantola agree surprisingly well. The value of Vegard is too low; the accuracy of his measurements are not stated. Glover has given the following equation for the lattice expansion of potassium chloride from 0 to 600° C.

$$\alpha = (34\cdot6\times10^{-6} + 3\cdot5\times10^{-8}\,t^\circ\,\mathrm{C.})$$

His estimate of error is $\pm0\cdot8\times10^{-6}$ which is about $\pm2\cdot5\%$.

A comparison of Glover's values with the macroscopic values of the author show that the latter are systematically higher than the former by about 4 to 5%. It should be mentioned that Kantola's X-ray value is greater by about the same amount than Glover's expansion coefficient value at 61° C. This difference may perhaps be due to the different specimens used by these investigators. The accuracy of the macroscopic measurements of the author is about 3%. It is noteworthy that though the specimens employed by the author and Glover were different, the difference between the two values of α is small and it is just on the limits of experimental error.

A comparison of the macroscopic expansion values of rock-salt and pure sodium chloride reveals, that the difference between the two values is wholly within the limit of error. This is in conformity with Glover's finding that small amount of impurities in crystals of KCl did not affect the expansion coefficient.

In conclusion, the author wishes to express his gratitude to Professor R. S. Krishnan for his kind interest and encouragement during the course of this work. He is also grateful to Dr. K. Vedam and Mr. C. P. Gopalakrishnan for supplying him with the specimens of sodium and potassium chlorides grown from melt in this laboratory.

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