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NO 346

THE THERMAL EXPANSION OF NaCl

AT HIGH PRESSURES AND TEMPERATURES

By Harry Hughes

Trace Elements Investigations Report 346

UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

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UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

January 23, 1959

AEC-222/9

Mr. James E. Reeves
Assistant Manager for Test Operations
Albuquerque Operations Office
U. S. Atomic Energy Commission
P. O. Box 5400
Albuquerque, New Mexico

Dear Mr. Reeves:

Transmitted herewith are 10 copies of TEI-346, "The thermal expansion of NaCl at high pressures and temperatures," by Harry Hughes, December 1958.

This report is part of our regular Geological Survey program, but we are transmitting it to the Commission in the TEI series as we believe it may be of interest to scientists working on Project GNOME. We plan to incorporate the information in TEI-346 with other material for publication by the Geological Survey.

Sincerely yours,

W. H. Bradley
Chief Geologist

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January 23, 1959

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Dr. Daniel R. Miller
Chemistry Branch
Division of Research
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Dan:

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This report is part of our regular Geological Survey program, but we are transmitting it to the Commission in the TEI series as we believe it may be of interest to scientists working on Project MICE. We plan to incorporate the information in TEI-346 with other material for publication by the Geological Survey.

Sincerely yours,

Andrew Brown

for W. H. Bradley
Chief Geologist

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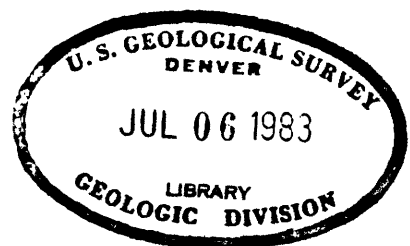
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THE THERMAL EXPANSION OF NaCl AT HIGH PRESSURES AND TEMPERATURES

By Harry Hughes

ABSTRACT

The thermal expansion of NaCl at high pressures and temperatures, is estimated by extrapolating high temperature compressibility data to high pressures using finite strain theory. The thermal expansion is apparently negative at pressures over 50,000 bars at 300°C and at higher pressures at other temperatures.

INTRODUCTION

Generally a substance becomes more compressible as its temperature is raised. If two equal masses of material at temperatures T_1 and T_2 ($T_1 > T_2$) and volumes V_1 and V_2 ($V_1 > V_2$ due to thermal expansion) then, because of the greater compressibility at the higher temperature, at sufficient pressure ($P > P'$, fig. 1) the additional compression is greater than the initially greater volume and the thermal expansion at these pressures is thus negative.

Experimental data on halite (NaCl) are more extensive than on most other minerals so that we can estimate under what conditions this effect occurs in salt.

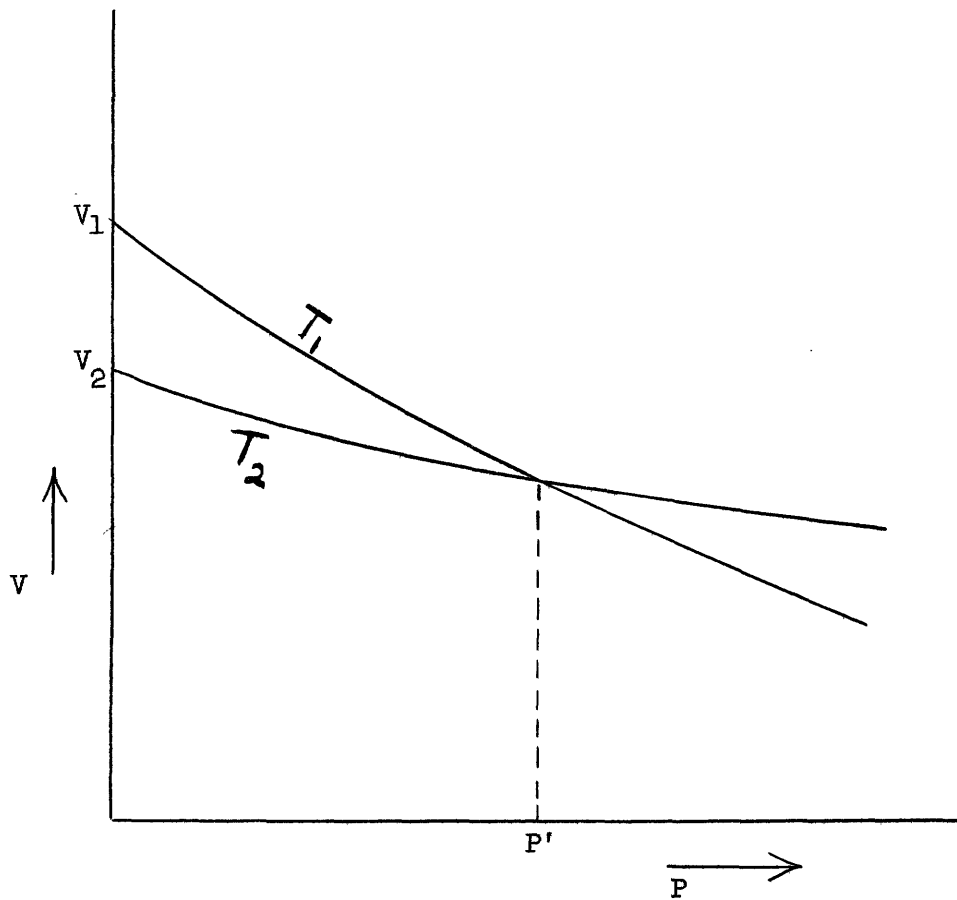


Figure 1. Effect of T and P
on V (diagrammatic)

CALCULATION

At low temperatures and moderate pressures the thermal expansion of salt has been measured directly by Bridgman (1940). From his measurements of compression at -80°C and 20°C (reproduced in table 1) it can be seen that the thermal expansion is reduced by a factor 2 at 50,000 bars pressure. Our problem is to extrapolate these results to higher pressures and temperatures.

We use the relation

$$\frac{\alpha}{\alpha_{p=0}} = 1 - P\beta_T \left[\frac{1}{\alpha\beta_T} \frac{\partial\beta_T}{\partial T} \right]_{p=0} \quad (1)$$

derived by Birch (1939) by integrating the fundamental relation

$$\left(\frac{\partial\alpha}{\partial P} \right)_T = - \left(\frac{\partial\beta_T}{\partial T} \right)_P \quad (\text{both equalling } \frac{1}{V} \frac{\partial^2 V}{\partial T \partial P}) \quad (2)$$

where α is the thermal expansion and β_T the isothermal compressibility.

Now the term in brackets in equation 1 is known from Bridgman's measurements at low temperatures, and at high temperatures can be determined from measurements of the adiabatic compressibility (Hunter and Seigel, 1942) by use of the thermodynamic relation $\beta_T = \beta_S (1 + T \alpha \gamma)$, γ being Gruneisen's constant. The data are shown in table 2. The other unknown in equation 1, β_T , can be estimated by using the relation

$$\beta_p = \alpha/\beta = (1+2f)^{5/2} (1+7 - 2 \xi f (2+9f)) \quad (3)$$

where f is a measure of the strain given by $V_0/V = (1+2f)^{3/2}$ and ξ is a small adjustable parameter. The theoretical and experimental support for the above equation is discussed extensively by Birch (1952).

Table 1.--Compression of NaCl (Bridgman, 1940)

Pressure (bars)	0	5,000	10,000	15,000	20,000	25,000	30,000	35,000	40,000	45,000	50,000
$-\Delta V/V_0$ at 20°C	0	.0192	.0365	.0523	.0664	.0798	.0919	.1029	.1130	.1223	.1309
$-\Delta V/V_0$ at -80°C	0	.0177	.0341	.0494	.0634	.0763	.0880	.0987	.1084	.1172	.1250
$V_{20^\circ} - V_{-80^\circ}$.0116	.0101	.0092	.0087	.0086	.0081	.0077	.0074	.0070	.0065	.0057

Figure 2 shows equation 3 graphically taking ξ as -0.3 (see below) and the resulting value of α/α_0 obtained from equation 1 taking the term in brackets as 5. Exact values for this term at different temperatures are shown in table 2 and the appropriate adjustment to the figure is readily made. To find the thermal expansion at any temperature and pressure, the strain produced by that pressure is first found from the lower curve (drawn from the relation

$$P \beta_{p=0} = 3f (1+2f)^{5/2} (1-2\xi - f) \quad (4)$$

a consequence of equation 3), and the value of α/α_0 at that strain is read for the values of $\beta_p = 0$ and $\left[\frac{1}{\alpha\beta} \frac{\partial \beta}{\partial T} \right]_{p=0}$ at the particular temperature. The resulting estimates of the thermal expansion are shown in table 3.

The accuracy of these values can be seen from equation 2 to depend on the estimate of the compressibility over the temperature-pressure field. The goodness of fit of the compressibility to equation 3 can be expressed in terms of the parameter ξ . Lazurus (1949) obtains -0.3 for this parameter, whereas Bridgman's measurements are best fitted by a value of -0.6 (Birch, 1954). Most substances have ξ very nearly zero (Birch, 1952), and all the determinations have been made near room temperature. An uncertainty of ± 0.3 in ξ does not appreciably change the estimated compressibility at small strains and affects it only ± 7.7 percent at strains of 20 percent (equation 3). This uncertainty also affects the strain produced by a given pressure (equation 4) but its principal effect is likely to be in the

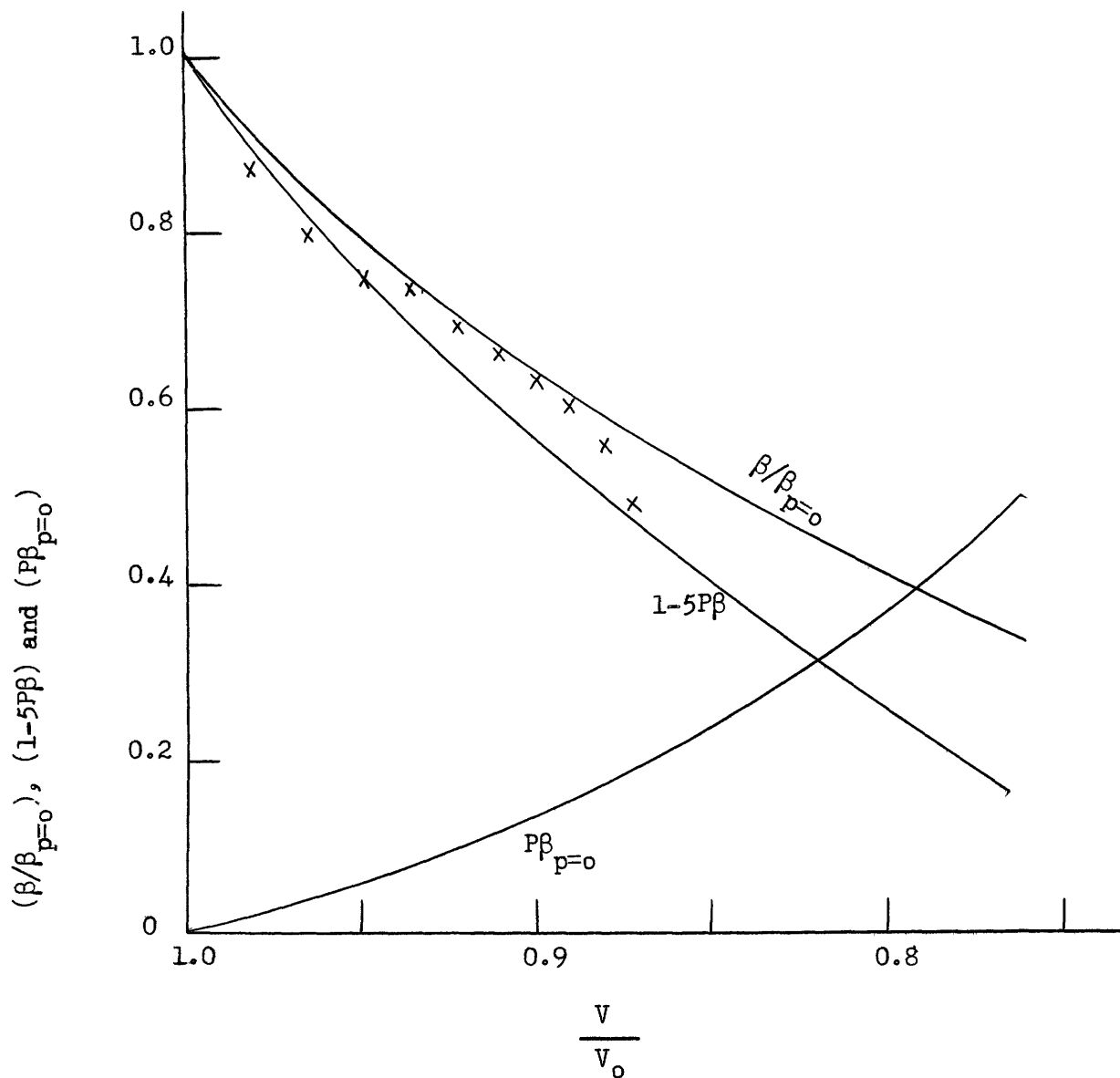


Figure 2. Compressibility, β , and thermal expansion, α , of NaCl as a function of compression. (x = measurements of α between -80°C and 20°C , ξ taken as -0.3)

Table 2.--Properties of NaCl at One Atmosphere (Hunter and Siegel, 1942;
Walther and others 1937)

T	$10^{13}\beta_s$	$10^6\alpha$	γ	$10^{13}\beta_T$	$\left(\frac{1}{\alpha\beta_T} \frac{\partial\beta_T}{\partial T}\right)$
(°K)	(cm ² /dyne)	(deg ⁻¹)		(cm ² /dyne)	
300	41.4	120	1.56	43.7	5.17
400	43.1	128	1.57	46.6	5.93
500	45.6	136	1.56	50.4	8.04
600	50.1	143	1.46	56.4	7.48
700	54.8	152	1.40	63.0	6.72
800	59.3	165	1.38	70.1	5.65
900	63.1	180	1.39	77.3	5.27
1000	65.7	201	1.50	85.5	

Table 3.--Estimated Values of the Thermal Expansion of NaCl ($\times 10^6$)°C⁻¹

T(°K)	Estimated value for indicated pressure (P), in bars						
	0	10 ⁴	2·10 ⁴	4·10 ⁴	6·10 ⁴	8·10 ⁴	10 ⁵
350	124	102	84	57	41	30	20
450	132	102	81	49	26	16	0
550	140	92	57	13	-15	-38	
650	148	99	62	15	-15	-36	
750	159	105	67	24	-6	-24	
850	173	119	87	42	16		
950	191	132	96	52	27		

value of the derivative $\partial\beta_T/\partial T$ if ϵ changes with temperature.

It can be seen from the rapid increase of β_T with temperature (table 2) that an increase in ϵ of only about 0.5 in a 100°C temperature interval is sufficient to prevent a positive value for $\partial\beta_T/\partial T$ (and thus a negative value for $\partial\alpha/\partial P$) but even this result holds only at the largest strains. As such large changes in ϵ are unlikely we conclude that the trend shown in table 3 is substantially correct.

It might appear from equation 1 that only the value of $\partial\beta_T/\partial T$ at zero pressure, where the value of ϵ is unimportant, determines the estimate of thermal expansion. However, this equation is valid only for $\epsilon = 0$ to allow for uncertainty in ϵ , the more fundamental equation 2 has to be considered as is done above.

SUMMARY AND APPLICATION

The estimates in Table 3 indicate that the thermal expansion of salt becomes negative first at temperatures of about 300°C (twice the Debye temperature) and at pressures above about 50,000 bars (or at greater compressions than about 17 percent). Higher pressures and compressions are needed at both higher and lower temperatures.

A pressure of 50,000 bars, corresponding to a depth of 100-200 kms. in the earth is far greater than that to which natural salt deposits are subjected but is small compared to the pressures deeper in the earth's mantle. A negative thermal expansion at high pressure may occur in other minerals for which no data are available. However, this effect is not likely to be geologically important. The mantle is assumed to have solidified from the bottom upwards, and this indicates

that the thermal expansion there was positive (contrast the freezing of a lake from the top downwards); this absence of a negative thermal expansion may be a consequence of the high temperatures in the mantle. The cooling of the earth, now most rapid at a depth of several hundred kilometers, seems to be associated with contractions leading to mountain building, so here again the geological evidence favors a normal (positive) thermal expansion.

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