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THE PHASE CHANGE IN POTASSIUM CHLORIDE

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ABSTRACT

Equations for the interaction of ions in an ionic crystal, developed earlier[1], which allow for the variation of compressibility with pressure, have been applied to calculation of properties connected with the phase transition of potassium chloride under pressure. The data used were only for the high pressure form of the compound. It was found that the calculated transition pressure was much closer to the observed value, if these equations were used; but simpler equations which use a constant compressibility were somewhat better in their calculated values for the lattice energy, molar volume, and change of volume with pressure for the low pressure form of potassium chloride (NaCl structure). It is concluded that, while calculations on these equations form a sensitive test of these equations, the fitting of the equation to the structure needs to be more elaborate.

INTRODUCTION

In a recent paper[1], the present writer discussed various equations for the calculation of the lattice energies of ionic crystals, equations which allowed for the variation of compressibility with pressure. These equations gave somewhat improved agreement with observed lattice energies, obtained from the Born–Haber cycle, as compared with simpler equations which do not take this variation into account. The present paper describes a further test of these equations in connection with the relative energies of the sodium chloride structure and of the cesium chloride structure for alkali halides, in particular for potassium chloride. It seems to be generally agreed that these two structures differ only slightly in energy, and consequently they might provide a fairly sensitive test of the validity of various equations.

Potassium chloride on compression at room temperature[2] undergoes a sudden decrease in volume at about 20 600 atm, which seems to arise from a transition from a sodium chloride to a cesium chloride structure[3]. A similar change is observed for other potassium and rubidium halides. The range of pressures used in the observations of the cesium chloride structure of potassium chloride is much more extensive than those for the sodium chloride structure. Consequently, in the calculations below, the adjustable constants in the various equations have been chosen to fit the data on the

CsCl structure, and then appropriately modified so as to apply to the NaCl structure. Potassium chloride was chosen, because, in addition to the availability of suitable data, it contains isoelectronic ions. It is therefore relatively plausible to assume that the repulsion energy of the ions varies somewhat similarly with distance, regardless of which pair of ions is being considered. In particular, when the repulsion energy was taken to be proportional to r^{-n}, where r is the distance between neighbours, it was assumed that the same exponent, n, applied to all repulsions. When the repulsion was taken to be proportional to $e^{-r/\rho}$, it was assumed that a single value of ρ could be used.

DATA ON POTASSIUM CHLORIDE

The molar volume of potassium chloride at various pressures had been found[2] to be

P	0	1	2	2.06	2.06	3	4	5	6
V	37.25	35.47	38.13	34.09	29.92	28.95	28.16	27.49	26.94

P	7	8	9	10	$\times 10^4$ atm
V	26.45	26.00	25.63	25.30	$\times 10^{-6}$ m^3

If, as before[1], the compressibility is assumed to vary with P according to

$$\beta = \beta_0 + \beta_1 P + \beta_2 P^2$$

a least squares fit of the data makes, for the CsCl structure, $\beta_0 = 4.124 \cdot 10^{-6}$ atm^{-1}; $\beta_1 = -4.2645 \cdot 10^{-11}$ atm^{-2}; $\beta_2 = 1.265 \cdot 10^{-16}$ atm^{-3}. The extrapolated volume at zero pressure is 32.23×10^{-6} m^3, corresponding to $r = 3.263 \times 10^{-10}$ m (CsCl structure).

Other quantities needed in the calculations are as follows. M and Q are defined by:

$$M = NAe^2 z_+ z_-, \text{ and } Q = \frac{9 V_0 r_e}{\beta_0},$$

where N is Avogadro's number, A is the Madelung constant, and the charges on the ions are $+ez_+$ and $-ez_-$. V_0 is the molar volume and r_e the distance of neighbouring ions, both at zero pressure. Compounds with the NaCl structure have $M = 2.42787 \cdot 10^{-4}$ J m; for the CsCl structure, $M = 2.44886 \cdot 10^{-4}$ J m mol^{-1}. Q for KCl (CsCl structure) is 23.256×10^{-4} J m mol^{-1}. Van der Waals energies were taken to be C'/r^6, where, if we use Mayer's values[4], for KCl, $C' = 4.1057 \cdot 10^{-53}$ J m^6 mol^{-1} for the CsCl structure; $C' = 2.7161 \cdot 10^{-53}$ J m^6 mol^{-1} for the NaCl structure.

Certain derived quantities are needed. These are:

$$D = C'/r_e^5$$

$$X = \frac{M + 6D}{r_e}$$

$$Y = \frac{2M+42D+Q}{r_e}$$

$$Z = \frac{6M+336D}{r_e} - \frac{27V_0(\beta_0^2+\beta_1)}{\beta_0^3}$$

$$W = \frac{24M+3024D}{r_e} + \frac{9V_0}{\beta_0^5}(2\beta_0^+ + 9\beta_1^2 + 27\beta_0^2\beta_1 + 18\beta_0\beta_z)$$

For KCl (CsCl structure) these are found to be: $D = 1.1093 \cdot 10^{-5}$ J m mol^{-1}; $X = 9.5435 \cdot 10^5$, $Y = 1.0055 \cdot 10^7$, $Z = 4.8158 \cdot 10^7$, $W = 2.8724 \cdot 10^8$, all in J mol^{-1}. These quantities will be used in eqns (5), (6) and (7) below.

The lattice energy of the sodium chloride structure is also a useful test for the validity of any equation. The "observed" value of this quantity, obtained from the Born–Haber cycle by means of data collected by Dasent[5], is -712 kJ.

EQUATIONS WITH TWO ADJUSTABLE CONSTANTS

The equations investigated will be numbered as in the previous paper[1].

Eqn (3): Born equation with Van der Waals term

$$E = -\frac{M}{r} - \frac{C'}{r^6} + \frac{B}{r^n}$$

As was shown earlier

$$n = \frac{Q+M+36D}{M+6D},$$

and it can easily be shown that

$$B = \frac{(M+6D)\, r_e^{n-1}}{n}$$

It was assumed that the repulsive term could be expanded to allow for the repulsions of ions at various distances by writing

$$\frac{B}{r^n} = B_0 \sum_i \frac{N_i}{(q_i r)^n}, \text{ or } B = B_0 \sum_i \frac{N_i}{q_i^n},$$

where there are N_i ions at distance $q_i r$ from any given ion, and r is the distance of nearest neighbours. This is an infinite series for B, though in practice a rapidly converging one. It was, however, decided to break it off after a few terms for two reasons: (i) the calculation is much simplified for a very small change in result; and (ii) it is probably more realistic to ignore the repulsion of remote ions, because intervening ions will interfere with this. Thus in the sequence of ions: + − +, it seems probable that the non-electrostatic repulsion of the outside ions will be reduced, possibly removed, by the presence of the middle ion. Further, for the present calculation, any errors from this will largely cancel in comparisons of the CsCl and NaCl structures, since the same assumption is made in both cases. It was decided to terminate the series, $\sum_i N_i/q_i^n$, after the terms:

$$\text{CsCl structure}\left\{\begin{array}{llll} N_i & 8 & 6 & 12 \\ q_i & 1 & \sqrt{\frac{4}{3}} & \sqrt{\frac{8}{3}} \end{array}\right.$$

$$\text{NaCl structure}\left\{\begin{array}{llll} N_i & 6 & 12 & 8 \\ q_i & 1 & \sqrt{2} & \sqrt{3} \end{array}\right.$$

These were chosen, in part, because in both cases the repulsions of 26 ions are considered. If $n = 10$, which is a typical value, and the series is not terminated, the total is 0.3% larger for the CsCl structure, and 0.5% larger for the NaCl structure. Hence, even if the supposition, that the non-electrostatic repulsion of remote ions is removed by intervening ions, is not correct, the error so introduced is small.

This allows us to calculate E for various values of r: we also need to calculate the pressure, which was obtained from $P = -\dfrac{\mathrm{d}E}{\mathrm{d}V} = \dfrac{1}{3V}\left(-r\dfrac{\mathrm{d}E}{\mathrm{d}r}\right)$. Hence, for eqn (5):

$$P = \frac{1}{3V}\left[-\frac{M}{r} - \frac{6C'}{r^6} + \frac{nB_0}{r^n}\sum_i \frac{N_i}{q_i^n}\right]$$

The method used was to calculate values of E and P at various values of r; the molar volume, given by $V = CNr^3$, was also calculated. A plot was then made of E against P, and also V against P; and from this interpolated values of E and V at various pressures could be found. This was done both for the CsCl and NaCl structures. Hence for the transition

KCl (NaCl structure) → KCl (CsCl structure)

values of ΔE and $P\Delta V$ could be calculated for each selected value of the pressure. In practice this was usually done for multiples of 10^4 atm. Since $\Delta H = \Delta E + P\Delta V$ (at constant P), values of ΔH could be found.

We really need values of ΔG, the free energy change, and this involves the entropy term, $T\Delta S$, which is not available for the CsCl structure of potassium chloride. It is, however, true that values for the absolute entropies of the alkali halides (see, for instance, ref. 5, p. 86) increase in a fairly regular way in going from lithium to cesium, or from fluoride to iodide, and the three salts with the CsCl structure are not out of line. There is some scatter in the values, but it seems safe to conclude that the different structure of the three cesium halides has not altered their absolute entropy at 298 K by more than a small amount. It is therefore probable that $T\Delta S$ for the phase change in KCl is also small, and the equilibrium is governed by the relative sizes of ΔE and $P\Delta V$.

When the equations given above were applied to KCl (CsCl structure), it was found that $n = 9.5357$, $B = 3.4821 \cdot 10^{-86}$ J m^n mol^{-1}. Hence $B_0 = 3.6144 \cdot 10^{-87}$ J m^n mol^{-1}. The results for E and V at various P, for both structures, are given in Table 1. This table also contains ΔE, $P\Delta V$, and ΔH for the transition from the NaCl to the KCl structure. Comments on these results will be made after the other equations have been applied.

TABLE 1

VALUES OF E AND V AT VARIOUS P, CALCULATED BY EQN (3)
All quantities are for 1 mol; quantities for the transition are in kJ.

P (atm)	*CsCl structure*		*NaCl structure*		*NaCl→CsCl structure*		
	V (m³)	*E (kJ)*	*V (m³)*	*E (kJ)*	ΔE	$P\Delta V$	ΔH
$0 \cdot 10^4$	$32.23 \cdot 10^{-6}$	−684.31	$37.05 \cdot 10^{-6}$	−704.29	19.98	0.0	19.98
1	31.10	−683.68	35.57	−703.52	19.84	−4.53	15.31
2	30.12	−682.30	34.34	−701.80	19.50	−8.55	10.95
3	29.32	−680.32	33.35	−699.36	19.04	−12.25	6.79
4	28.65	−677.86	32.56	−696.42	18.56	−15.85	2.71
5	28.06	−675.24	31.86	−693.20	17.96	−19.25	−1.29
6	27.54	−672.39	31.22	−689.72	17.33	−22.37	−5.04
7	27.07	−669.26	30.67	−685.98	16.72	−25.53	−8.81
8	26.65	−666.04	30.15	−682.12	16.08	−28.37	−12.29
9	26.27	−662.80	29.69	−678.24	15.44	−31.19	−15.75
10	25.93	−659.52	29.28	−674.34	14.82	−33.94	−19.12

Eqn (4): Born-Mayer equation with Van der Waals term

$$E = -\frac{M}{r} + \frac{C'}{r^6} + B' \mathrm{e}^{-r/\rho}$$

As was shown earlier[1],

$$\frac{r_e}{\rho} = \frac{Q + 2M + 42D}{M + 6D}$$

where r_e is the equilibrium distance. This was modified to include separately the repulsions of various neighbours:

$$E = -\frac{M}{r} - \frac{C'}{r^6} + B'_0 \sum_i N_i \mathrm{e}^{-q_i r/\rho}$$

The pressure is given by

$$P = \frac{1}{3V}\left[-\frac{M}{r} - \frac{6C'}{r^6} + B'_0 \sum_i N_i \frac{q_i r}{\rho} \mathrm{e}^{-q_i r/\rho}\right]$$

B'_0 was found by putting $P=0$ at $r=r_e$, and using the value of r_e/ρ as given above. The same number of neighbouring ions has been considered as for eqn (3).

From data for KCl (CsCl structure) we get $r_e/\rho = 10.5357$, or $\rho = 0.30975 \times 10^{-10}$ m; and $B'_0 = 3.6334 \times 10^8$ J mol^{-1}. As before, values of E, V and P for various r were obtained for both structures. From plots of these results values of V and E at various P were obtained, and these are given in Table 2, which also contains calculated values of ΔE, $P\Delta V$ and ΔH for the transition from the NaCl to the CsCl structure of potassium chloride.

TABLE 2

VALUES OF E AND V AT VARIOUS P, CALCULATED BY EQN (4)

P (atm)	*CsCl structure*		*NaCl structure*		*NaCl→CsCl structure*		
	V *(m³)*	E *(kJ)*	V *(m³)*	E *(kJ)*	ΔE	$P\Delta V$	ΔH
$0 \cdot 10^4$	$32.23 \cdot 10^{-6}$	−695.66	$36.83 \cdot 10^{-6}$	−712.63	16.97	0.0	16.97
1	31.09	−695.03	35.25	−711.82	16.79	−4.22	12.37
2	30.15	−693.76	34.05	−710.04	16.28	−7.90	8.38
3	29.39	−691.92	33.01	−707.48	15.56	−11.00	4.56
4	28.69	−689.38	32.14	−704.42	15.04	−13.98	1.06
5	28.06	−686.59	31.36	−700.98	14.39	−16.72	−2.33
6	27.52	−683.56	30.71	−697.30	13.74	−19.39	−5.65
7	27.03	−680.26	30.10	−693.32	13.06	−21.77	−8.71
8	26.59	−676.92	29.54	−689.16	12.24	−23.91	−11.67
9	26.21	−673.57	29.05	−684.96	11.39	−25.90	−14.51
10	25.85	−670.20	28.63	−680.76	10.56	−28.17	−17.61

Eqn (5)

This equation was

$$E = -\frac{M}{r} - \frac{C'}{r^6} + (B + Gr + Hr^2)\, e^{-r/\rho}$$

As was shown earlier[1], if we define X, Y, Z, and W as was given above, and $u = r_e/\rho$, then $Xu^3 - 3Yu^2 + 3Zu - W = 0$. This was used to find u, and hence ρ. Equations were also given earlier from which it is possible to evaluate B, G and H from the known values of X, Y, Z, W and u. These equations, slightly rearranged from the earlier paper, are:

$$Bu + Gr_e(u-1) + Hr_e^2(u-2) = Xe^u$$

$$Bu^2 + Gr_e(u^2-2u) + Hr_e^2(u^2-4u+2) = Ye^u$$

$$Bu^3 + Gr_e(u^3-3u^2) + Hr_e^2(u^3-6u^2+6u) = Ze^4$$

In order to make eqn (5) applicable to either structure, it was assumed that the constants B, G, and H could be expanded as follows

$$B = B_0 \sum_i N_i$$

$$G = G_0 \sum_i N_i q_i$$

$$H = H_0 \sum_i N_i q_i^2$$

where N_i is the number of ions at distance $q_i r$. In both cases the sums were taken over the first 26 ions. These expressions sum the repulsions for the various ions, and the resulting expressions for E and P were

$$E = -\frac{M}{r} - \frac{C'}{r^6} + \sum_i N_i [B_0 + G_0 q_i r + H_0 (q_i r)^2]\, e^{-q_i r/\rho}$$

$$P = \frac{1}{3V}\left[-\frac{M}{r} - \frac{6C'}{r^6} + \sum_i N_i q_i \frac{r}{\rho} \{B_0 + G_0(q_i r - \rho) + H_0 q_i r(q_i r - 2\rho)\}\, e^{-q_0 r/\rho}\right]$$

Data on the CsCl structure of KCl make $u = 26.2829$, $B_0 = 8.3402 \times 10^{16}$ J mol^{-1}, $G_0 = -5.7727 \times 10^{26}$ J m^{-1} mol^{-1}, and $H_0 = 1.0052 \times 10^{36}$ J m^{-2} mol^{-1}. From these, the values of E and V for different P were obtained, and are given in Table 3, which also contains the calculated ΔE, $P\Delta V$, and ΔH for the transition.

TABLE 3

VALUES OF E AND V AT VARIOUS P, CALCULATED BY EQN (5)

P (atm)	*CsCl structure*		*NaCl structure*		*NaCl→CsCl structure*		
	V (m³)	*E (kJ)*	*V (m³)*	*E (kJ)*	ΔE	$P\Delta V$	ΔH
$0 \cdot 10^4$	$32.23 \cdot 10^{-6}$	−717.46	$36.68 \cdot 10^{-6}$	−723.96	6.50	0.0	6.50
1	31.06	−716.81	35.30	−723.40	6.59	−4.30	2.29
2	30.07	−715.36	34.47	−722.03	6.67	−8.92	−2.25
3	29.24	−713.25	33.87	−720.62	7.37	−14.07	−6.70
4	28.59	−710.87	33.40	−719.12	8.25	−19.49	−11.24
5	28.02	−708.44	33.02	−717.40	8.96	−25.33	−16.37
6	27.54	−706.00	32.70	−715.66	9.66	−31.37	−21.71
7	27.15	−703.52	32.47	−713.90	10.38	−37.73	−27.35
8	26.85	−701.02	32.25	−712.14	11.12	−43.77	−32.65
9	26.58	−698.50	32.04	−710.38	11.88	−49.97	−38.09
10	26.35	−695.98	31.83	−708.62	12.64	−55.53	−42.89

Eqn (6)

This equation was

$$E = -\frac{M}{r} - \frac{C'}{r^6} + \left(B + \frac{G}{r} + \frac{H}{r^2}\right) e^{-r/\rho}$$

As was shown earlier[1],

$$Xu^6+(14X-3Y)u^5+(78X-36Y+3Z)u^4+(204X-168Y+30Z-W)u^3+$$
$$+(264X-360Y+108Z-8W)u^2+(144X-360Y+168Z-18W)u-$$
$$-144Y+96Z-12W=0$$

where X, Y, Z, W and u are defined as for eqn (5). u is found from this equation. B, G, and H can be found from the equations, which are slight rearrangements of those given earlier:

$$\begin{aligned}
Bu+\frac{G}{r_e}(u+1)+\frac{H}{r_e^2}(u+2) &= Xe^u\\
Bu^2+\frac{G}{r_e}(u^2+2u+2)+\frac{H}{r_e^2}(u^2+4u+6) &= Ye^u\\
Bu^3+\frac{G}{r_e}(u^3+3u^2+6u+6)+\frac{H}{r_e^2}(u^3+6u^2+18u+24) &= Ze^u
\end{aligned}$$

The effect of either the NaCl or CsCl structure was accomodated as for eqn (5) by summing the repulsive energy over 26 neighbouring ions. The equations used were:

$$E=-\frac{M}{r}-\frac{C'}{r^6}+\sum_i N_i\left(B_0+\frac{G_0}{q_i r}+\frac{H_0}{q_i^2 r^2}\right)e^{-q_i r/\rho}$$

$$P=\frac{1}{3V}\left[-\frac{M}{r}-\frac{C'}{r^6}+\sum_i N_i\left\{B_0\frac{q_i r}{\rho}+\frac{G_0}{q_i r}\left(\frac{q_i r}{\rho}+1\right)+\right.\right.$$
$$\left.\left.+\frac{H_0}{q_i^2 r^2}\left(\frac{q_i r}{\rho}+2\right)\right\}e^{-q_i r/\rho}\right]$$

Data on the CsCl structure of KCl make $u=24.3837$, $B_0=1.6350\cdot10^{16}$ J mol^{-1}, $G_0=-9.3991\cdot10^6$ J m mol^{-1}, and $H_0=1.3590\cdot10^{-3}$ J m^2 mol^{-1}. The values of E and V at various P, obtained from these, are given in Table 4, which also contains ΔE, $P\Delta V$ and ΔH as before.

Eqn (7)

This equation was

$$E=-\frac{M}{r}-\frac{C'}{r^6}+\frac{B}{r^n}+\frac{G}{r^{n+w}}+\frac{H}{r^{n+2w}}$$

where w is an arbitrarily selected, small integer. As was shown earlier, n can be found

TABLE 4

VALUES OF E AND V AT VARIOUS P, CALCULATED FROM EQN (6)

P (atm)	*CsCl structure*		*NaCl structure*		*NaCl→CsCl structure*		
	V (m^3)	E (kJ)	V (m^3)	E (kJ)	ΔE	$P\Delta V$	ΔH
$0\cdot 10^4$	$32.23\cdot 10^{-6}$	−717.26	$36.64\cdot 10^{-6}$	−723.89	6.63	0.0	6.63
1	31.04	−716.68	35.29	−723.34	6.66	−4.31	2.35
2	30.07	−715.24	34.48	−722.00	6.76	−8.94	−2.18
3	29.23	−713.04	33.90	−720.55	7.51	−14.20	−6.69
4	28.57	−710.62	33.43	−718.96	8.24	−19.70	−11.46
5	27.99	−708.15	33.07	−717.33	9.18	−25.74	−16.56
6	27.56	−705.62	32.78	−715.67	10.05	−31.73	−21.68
7	27.18	−703.14	32.52	−713.97	10.83	−37.88	−27.05
8	26.82	−700.74	32.28	−712.23	11.49	−44.26	−32.77
9	26.57	−698.46	32.06	−710.46	12.00	−50.06	−38.06
10	26.40	−696.20	31.88	−708.70	12.50	−55.53	−43.03

from:

$$Xn^3+(3wX+3X-3Y)\,n^2+(2w^2X+6wX+3X-6wY-9Y+3Z)\,n+$$
$$+(2w^2+3w+1)\,X-(2w^2+9w+7)\,Y+(3w+6)\,Z-W=0$$

The quantities B, G and H can be found from the equations

$$nBr_c^{2w}+(n+w)\,Gr_c^{w}+(n+2w)\,H = Xr_c^{n+2w}$$
$$n(n+1)\,Br_c^{2w}+(n+w)\,(n+w+1)\,Gr_c^{w}+(n+2w)\,(n+2w+1)\,H = Yr_c^{n+2w}$$
$$n(n+1)\,(n+2)\,Br_c^{2w}+(n+w)\,(n+w+1)\,(n+w+2)\,Gr_c^{w}+(n+2w)\times$$
$$\times(n+2w+1)\,(n+2w+2)\,H = Zr_c^{n+2w}$$

The effect of different structures was introduced as before, and it was assumed that:

$$E = -\frac{M}{r}-\frac{C'}{r^6}+\sum_i N_iB_0(q_ir)^{-n}+G_0(q_ir)^{-n-w}+H_0(q_ir)^{-n-2w}$$

and hence

$$P = \frac{1}{3V}\left[-\frac{M}{r}-\frac{6C'}{r^6}+\sum_i N_iB_0n(q_ir)^{-n}+G_0(n+w)\,(q_ir)^{-n-w}+\right.$$
$$\left.+H_0(n+2w)\,(q_ir)^{-n-2w}\right]$$

If $w=1$, it was found, from the data on the CsCl structure of KCl, that $B_0 = 9.6952\cdot 10^{-237}$ J m^n mol^{-1}, $G_0=-5.6343\cdot 10^{-246}$ J m^{n+1} mol^{-1}, and $H_0=8.2204\cdot 10^{-256}$ J m^{n+2} mol^{-1}. The value of n was 25.4832. The same results as for the other equations are given in Table 5. It was found in a preliminary calculation that the size of w had little effect, so this was not pursued.

TABLE 5

VALUES OF E AND V AT VARIOUS P, CALCULATED FROM EQN (7), WITH $w=1$

P (atm)	*CsCl structure*		*NaCl structure*		*NaCl→CsCl structure*		
	$V (m^3)$	E (kJ)	$V (m^3)$	E (kJ)	ΔE	$P\Delta V$	ΔH
$0 \cdot 10^4$	$32.23 \cdot 10^{-6}$	−714.14	$36.43 \cdot 10^{-6}$	−722.80	8.66	0.0	8.66
1	30.99	−713.44	35.30	−722.24	8.80	−4.37	4.43
2	29.94	−711.94	34.66	−721.28	9.34	−9.57	−0.23
3	29.08	−709.72	34.18	−720.16	10.44	−15.50	−5.06
4	28.40	−707.42	33.84	−718.82	11.40	−22.05	−10.65
5	27.91	−705.18	33.53	−717.42	12.24	−28.47	−16.23
6	27.50	−703.00	33.25	−715.98	12.98	−34.96	−21.98
7	27.17	−700.84	33.01	−714.52	13.68	−41.42	−27.74
8	26.90	−698.78	32.83	−713.04	14.26	−48.07	−33.81
9	26.67	−696.78	32.66	−711.62	14.84	−54.62	−39.78
10	26.50	−694.86	32.50	−710.22	15.36	−60.80	−45.44

DISCUSSION

The results obtained above are summarized in Table 6. This table contains, firstly, the calculated transition pressure, on the assumption that $\Delta S = 0$. Alternatively this is the transition pressure for 0 K. Reasons were given above for supposing that ΔS is small, and it can be seen from the above results that it would require an entropy difference between 11.4 J deg^{-1} mol^{-1} (for eqn (4)) and 16.5 J deg^{-1} mol^{-1} (for eqn (7)) to change the calculated transition pressure by 10^4 atm at 25°C. Secondly, the table contains the lattice energy, the molar volume at zero pressure, and the change

TABLE 6

COMPARISON OF OBSERVED PROPERTIES WITH THOSE CALCULATED BY VARIOUS EQUATIONS

Equation	*P (transition) (atm)*	*NaCl structure*		
		$V (m^3)$	E (kJ)	$-\Delta V$ (0 to $2 \cdot 10^4$ atm) (m^3)
Observed	20 600	$37.25 \cdot 10^{-6}$	−712	$3.13 \cdot 10^{-6}$
3	46 800	37.05	−704.3	2.71
4	43 100	36.83	−712.6	2.78
5	15 000	36.68	−724.0	2.21
6	15 200	36.64	−723.9	2.16
7 ($w = 1$)	19 500	36.43	−722.8	1.77

in volume on applying a pressure of 20 000 atm, all for the NaCl structure of potassium chloride.

It should be emphasized that none of the calculated values use any data for the NaCl structure, excepting only the arrangement of ions. All the data used were for the high pressure form.

Inspection of Table 6 shows a rather mixed situation. The calculated transition pressure is much improved by taking an equation with more adjustable constants, and fitting these to the change of compressibility with pressure. On the other hand the molar volume, the lattice energy, and the change in volume at 20 000 atm are not improved; in fact the reverse is true. Equation (3) gives the best agreement with the molar volume, and eqn (4) of the other two quantities. These simple equations give fairly reasonable agreement with experiment for these quantities.

The conclusion must be that a more sophisticated approach must be taken to fitting the pressure/volume data to an appropriate equation. This can be done in various ways, even apart from the obvious resource of introducing more adjustable constants. Firstly, the method of allowing for the variation of compressibility with pressure is somewhat arbitrary, and presumably could be improved. Secondly, a distinction between the cations and anions (apart from their charge) could be introduced, and each type of interaction could be treated separately. It is hoped to investigate these potential improvements, and also to extend the calculation to other potassium and rubidium salts. It can, perhaps, also be concluded that this transition affords a fairly sensitive way of assessing the validity of these equations.

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