

TABLE 1

AGREEMENT OF EXPERIMENTAL AND CALCULATED PARAMETERS
IN PRESSURE DISTRIBUTION ANALYSIS

Sample	P_m/P_a		
	20 kbar		40 kbar
	exper.	calc.*	exper.
Pure Ni(DMG) ₂	2.0		
Pure TiBr	2.0	1.96	
Ni(DMG) ₂ in KBr(1:2)**	1.85	1.90	
Ni(DMG) ₂ in NaCl(1:2)	1.80	1.95	1.43
Ni(DMG) ₂ in NaCl(1:3)	2.0	1.95	
Ni(DMG) ₂ in NaCl(1:3) poor alignment	1.60	1.95	

TABLE 2

Sample	r_a/r_o		
	20 kbar		40 kbar
	exper.	calc.*	exper.
Pure Ni(DMG) ₂	0.70		
Pure TiBr	0.68	0.61	
Ni(DMG) ₂ in KBr(1:2)	0.52	0.60	
Ni(DMG) ₂ in NaCl(1:2)	0.69	0.62	0.55
Ni(DMG) ₂ in NaCl(1:3)	0.62	0.62	
Ni(DMG) ₂ in NaCl(1:3) poor alignment	0.70	0.62	

* calculation based on the pure alkali halide
**phase transition at 18 kbar with a 10% volume decrease makes calculation difficult and causes a steeper pressure gradient

will be seen that the reference compressibility can be chosen as the compressibility at atmospheric pressure, a value which can be more accurately determined than perhaps at any other pressure and by independent methods.

It has been shown earlier that

$$-2r \, dr/dP = \beta / (\Delta V_a/V_o) = d(1 - r^2)/dP \quad (6)$$

In Fig. 18 it was seen that a plot of $1-r^2$ versus pressure is not linear. Equation (6) requires nonlinearity since β is pressure dependent. Now, as the pressure approaches 1 atm (at the edge of the cell) $\beta \rightarrow \beta_o$, the compressibility at 1 atm.

Let us consider a plot, similar to that in Fig. 18 but with pressure on the abscissa since β is dependent on pressure. This is an experimental pressure gradient determined on a sample of nickel dimethylglyoxime diluted with 2 parts sodium chloride at 20 kbar applied pressure. β_o for sodium chloride is known to be 4.1×10^{-6} at 20°. The slope of the experimental plot at the origin was found to be $1/17050 = 0.00586$, so that

a (V_a/V_o) value of 0.070 is required to give

$$\beta_o = [d(1 - r^2)/dP]_{o, \text{exper}} [\Delta V_a/V_o] \quad (7)$$

$$\beta_o = 4.1 \times 10^{-6}$$

This value of $\Delta V_a/V_o$ is then used to convert the slopes at other points along the curve to β -values, since relation (7) is applicable at any pressure as well as at 1 atm. The points so calculated from the slopes are indicated in the upper part of the figure. The solid line is a plot of compressibility of pure sodium chloride calculated from $\Delta V/V_o$ data of Bridgman (18). The agreement is surprisingly good but one must remember that β does not change as rapidly with pressure as $\Delta V/V_o$ and the experimental points cannot be determined very accurately from the slopes.

The agreement with the literature compressibility values is apparently real since the pressure gradient curve for the same sample at 40 kbar gives similar results although the spread is greater, due perhaps to a less accurately known pressure profile. (These particular radial profiles were determined from only 6 experimental measurements; more points are usually required to get smooth profiles.)

Although the method appears to work fairly well, some concern should be shown about a number of problems. We would not, off hand, expect a matrix with 1 part nickel dimethylglyoxime and 2 parts sodium chloride to have exactly the same compressibility as sodium chloride. On this basis, the agreement would appear to be fortuitous. On the other hand, it appears, from qualitative observations made in this laboratory over a period of a year or two, that when a substance is diluted with 30 percent or more of a less compressible material the matrix behaves much the same as the less compressible material alone. It is rather difficult to imagine that the compressibility would not be affected by a minor component concentration of 33 percent. This is an interesting problem which must be solved before further quantitative work can be done.

The determination of slopes from a curve is neither convenient nor very accurate. If this work is continued, a large number of experimental points should be taken along the radius of near-perfectly aligned diamonds in order to obtain a smooth radial profile. A computer should be used to calculate the best curve using the best known compressibility-pressure relation. The computer should be instructed to evaluate the experimental slope at 1 atm and from a given value of β_o , com-