

see, for example, Tosi (1964) and Born and Huang (1954) each of which have an extensive bibliography.

Again, temperature effects are included by adding a "thermal pressure", i.e., a vibration energy term is included in the free energy. The Mie-Gruneisen equation is most common with  $\gamma$  assumed as a function of volume only. The appropriate  $\gamma$  in the Mie-Gruneisen equation is essentially temperature independent as shown by a direct calculation of the volume dependence of frequencies of the modes of vibration (Arenstein, et al., 1963).

Decker (1966) applied this theory for NaCl specifically to the problem of pressure calibration, particularly when the high pressure system was to be used at high temperatures. His equation was not considered as a "calibration" but was hopefully to be used to make temperature corrections to the pressure calibration once a room temperature isotherm was known. However, the calculated pressure versus volume agreed very well with Bridgman's (1945) isothermal measurements on NaCl and also with high pressure shock data (Alt'shuler, et al., 1960; Christian, 1957). More recently, it has been shown to give pressures accurate to 3 percent to 300 kbar (McWhan, 1967; Weaver, et al., 1967) when NaCl is compared with MgO for which the pressures can be confidently calculated from the equations of finite strain. The agreement is even better when the recent value of the initial compressibility of NaCl is used in the theoretical calculation (Decker, 1971; Chang, 1965; Slagle and McKinstry, 1967).

Because of the wide use of NaCl as a pressure standard, we give a comparison of various experimental and theoretical equations of state for this substance in the following section.

Compression data for NaCl have been based on: (1) shock compression studies by Christian (1957), Alt'shuler, et al., (1960), Lombard (1961), and Fritz, et al., (1968); (2) theoretical equation of state (based on the Mie-Gruneisen equation of state) by Decker (1971); (3) the Murnaghan equation of state employing ultrasonic bulk modulus data by Anderson (1966); (4) x-ray diffraction measurements by Perez-Albuerne and Drickamer (1965); (5) comparisons of molar volumes of NaCl and MgO by x-ray diffraction (McWhan, 1967; Weaver, et al., 1967). The results of these studies are not all in good agreement as shown in table 13. Therefore, some evaluation of these data are required before NaCl can be used as a pressure standard.

1. The shock Hugoniot data of Christian, Alt'shuler, et al., and Lombard are in fair agreement. Isothermal compression values based on shock data by Christian and Fritz, et al., differ by only 3 percent at 200 kbar. The recent data by Fritz, et al. can probably be considered the most reliable.

2. Decker's equation of state is sensitive to the zero pressure compressibility of NaCl. The values for pressure versus compression which he reported in his 1966 paper were based on a zero pressure isothermal compressibility of  $4.27 \times 10^{-3}$  kbar<sup>-1</sup>. The recent determinations of the zero pressure compressibility of NaCl by Chang (1965), Slagle and McKinstry (1967), and Drabble and Strathen (1967) indicate that the best value is  $4.22 \pm 0.01 \times 10^{-3}$  kbar<sup>-1</sup>. Decker (1971) has recalculated pressure versus compression based on this new value. (See table 14.)

Weaver, et al. (1968) have also calculated the volume-pressure relationship of NaCl using the Hildebrand and Mie-Gruneisen equations of state. They evaluated

TABLE 13. Reported pressure-volume relationships for NaCl (pressure in kbar)

Reference and temperature	Specific volume ( $V/V_0$ )	Pressure (kbar)							
		1.00	0.95	0.90	0.85	0.80	0.75	0.70	0.65
Christian (1957)	Hug <sup>a</sup>	0			61	100	152	221	(310)
	20 <sup>b</sup>	0			58	93	138	194	(260)
Alt'shuler, et al. (1960)	Hug <sup>a</sup>	0			62	98	149	214	316
Lombard (1961)	Hug <sup>a</sup>	0				102	154	224	340
Decker (1966)	25	0	13.6	31.7	55.8	88.2	131.6	192.1	275.0
Anderson (1966)	25	0	14	33	61	100	160	252	394
Perez-Albuerne & Drickamer (1965)	25	0	14	32	58	93	141	202	(290)
Weaver, et al. (1968a)	25	0	13.8	32.3	57.2	90.9	136.6	199.2	286
Decker (1968)	25	0	13.8	32.2	57.1	90.5	135.8	199.4	287.3
Fritz, et al. (1968)	25 <sup>b</sup>	0	14.0	33.1	59	94	140.9	203.2	Q
	25 <sup>b</sup>							203.7	292.1 L

<sup>a</sup> Shock Hugoniot uncorrected for temperature.

<sup>b</sup> Shock Hugoniot corrected to isotherm.

( ) Extrapolated values.

Q Quadratic fit.

L Linear fit.

TABLE 14. Calculated pressures vs. compression for NaCl at 25 °C

Compression		Pressure (kbar)	Compression		Pressure (kbar)
Linear $-\Delta a/a_0$	Volume $-\Delta V/V_0$		Linear $-\Delta a/a_0$	Volume $-\Delta V/V_0$	
0.001	0.0030	0.71	0.068	0.1904	83.79
0.002	0.0059	1.44	0.070	0.1956	87.72
0.004	0.0119	2.93	0.072	0.2008	91.75
0.006	0.0178	4.46	0.074	0.2059	95.90
0.008	0.0238	6.04	0.076	0.2111	100.17
0.010	0.0297	7.67	0.078	0.2162	104.57
0.012	0.0355	9.36	0.080	0.2213	109.08
0.014	0.0414	11.09	0.082	0.2263	113.72
0.016	0.0472	12.88	0.084	0.2314	118.50
0.018	0.0530	14.72	0.086	0.2364	123.40
0.020	0.0588	16.62	0.088	0.2414	128.45
0.022	0.0645	18.58	0.090	0.2464	133.64
0.024	0.0702	20.60	0.092	0.2513	138.97
0.026	0.0759	22.68	0.094	0.2563	144.45
0.028	0.0816	24.82	0.096	0.2612	150.85
0.030	0.0873	27.03	0.098	0.2661	155.08
0.032	0.0929	29.30	0.100	0.2710	161.83
0.034	0.0985	31.64	0.102	0.2758	167.95
0.036	0.1041	34.05	0.104	0.2806	174.24
0.038	0.1097	36.53	0.106	0.2854	180.70
0.040	0.1152	39.09	0.108	0.2902	187.35
0.042	0.1207	41.72	0.110	0.2950	194.17
0.044	0.1262	44.43	0.112	0.2997	201.19
0.046	0.1317	47.22	0.114	0.3044	208.40
0.048	0.1371	50.09	0.116	0.3091	215.81
0.050	0.1426	53.04	0.118	0.3138	223.42
0.052	0.1480	56.08	0.120	0.3185	231.25
0.054	0.1534	59.21	0.122	0.3231	239.29
0.056	0.1587	62.43	0.124	0.3277	247.55
0.058	0.1641	65.74	0.126	0.3323	256.03
0.060	0.1694	69.15	0.128	0.3369	264.76
0.062	0.1747	72.66	0.130	0.3414	273.72
0.064	0.1799	76.26	0.132	0.3460	282.92
0.066	0.1852	79.97	0.134	0.3505	292.38

the parameter in the Born-Mayer repulsive potential using the zero pressure compressibility given by Slagle and McKinstry. Their results are virtually the same as those of Decker. Weaver (1968) has compared the three NaCl pressure scales of Fritz, et al. (1968), Decker (1968), and Weaver, et al. (1968) and suggests some explanations for the discrepancies between them. However, these discrepancies are at most the same order of magnitude as the uncertainties due to the determinations of the lattice parameters by x-ray diffraction.

3. Anderson (1966) used the Murnaghan equation of state with the bulk modulus and its pressure derivative based on sonic velocity measurements up to 3 kbar by Bartels and Schuele (1965). The Murnaghan equation, which is valid when the bulk modulus is a linear function of pressure, yields results that deviate drastically from direct experimental data at compressions exceeding  $V/V_0=0.85$ . Therefore, the Murnaghan equation should not be used for compressions exceeding  $V/V_0=0.85$ .

4. Perez-Albuerné and Drickamer (1965) determined the compression of NaCl by x-ray diffraction employing silver and molybdenum as pressure standards. They used the shock compression data to calculate pressure from the molar volume of the silver and molybdenum. The compression data for NaCl thus obtained are in agreement with the Hildebrand equation of state employing parameters evaluated at low pressure.

TABLE 15. Reported pressure-volume relationships for MgO (pressure in kbar)

Reference and temperature	Specific volume ( $V/V_0$ )	Pressure (kbar)				
		1.000	0.950	0.925	0.900	0.875
Perez-Albuerné & Drickamer (1965)	25	0	103	161	229	308
Anderson & Schreiber (1965)	25	0	96	154	220	298
Anderson & Andreatch (1965)	25	0	92	149	215	292
McQueen & Marsh (1966)	Hug <sup>a</sup>	0	.....	.....	212	292

<sup>a</sup> Shock Hugoniot uncorrected for temperature.

5. Weaver, et al. (1967) used MgO as a pressure internal standard to determine the compression of NaCl by x-ray diffraction. MgO was chosen because compression data from four different sources (table 15) show much less scatter than the NaCl compression data. Shock compression results of McQueen and Marsh (1966) agree within 2 percent with data calculated by the Murnaghan equation in which the bulk modulus and its derivative were obtained by sonic velocity measurements on a single crystal (Anderson and Andreatch, 1965) and a polycrystalline sample (Anderson and Schreiber, 1965). Perez-Albuerné and Drickamer (1965) used niobium as a pressure standard to obtain compression data for MgO by x-ray diffraction. Their values are consistently higher than those from the other methods. The method by which the niobium shock data were corrected from the Hugoniot to the 25 °C isotherm is not discussed in their paper and it is possibly the source of the discrepancy.

Weaver, et al. (1967) chose to use the MgO compression data based on the polycrystalline sonic velocity measurements for their pressure determination. It is interesting to note that had they chosen the single crystal determination of Anderson and Andreatch (1965) or the shock data of McQueen and Marsh (1966), their pressures would be about 2 percent lower but would still agree within 1 percent with the NaCl pressure values of Decker (1971) and Fritz, et al. (1968).

McWhan (1967) also made molar volume comparisons between MgO and NaCl by high pressure x-ray diffraction up to 135 kbar. These are in excellent agreement with the measurements by Weaver, et al.

#### 4.2. Experimental Techniques for P-V-T Measurements

This section deals with experimental techniques capable of determining and utilizing relationships