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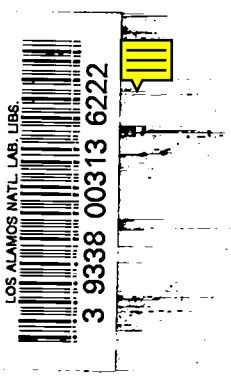

A COMPUTATIONALLY EFFICIENT EXPRESSION FOR THE ZERO-TEMPERATURE ISOTHERM IN EQUATIONS OF STATE

by

B. I. Bennett

ABSTRACT

A variation on the Barnes' modified Morse potential is given with two methods for determining empirical parameters. The new expression does not require the evaluation of a numerical integral to obtain the internal energy of the solid. Hugoniots computed using these two methods are compared with experimental data.

INTRODUCTION

A pair of expressions were proposed by J. F. Barnes in reference 1 for the zero-temperature pressure and internal energy of a solid. One of the expressions was selected to pursue that investigation and that expression required one to numerically evaluate an exponential integral to obtain the internal energy. It is the purpose of this work to explore the use of the discarded expression as applied to the analysis of shock data since no numerical integration is necessary. This expression should be computationally more efficient.

Two different schemes are used to evaluate the empirical parameters in the expression. The first approach uses the asymptotic limit of Thomas-Fermi theory to obtain the parameters and the second approach uses the theoretical values of cohesive energy to evaluate the parameters.

THE MODIFIED MORSE POTENTIAL

The alternate expression that was proposed in Reference 1 for a modified Morse potential for a solid was:

$$E'_M(\eta) = L\left[\eta^{\frac{2}{3}} e^{b_r \nu} - 2e^{b_a \nu}\right], \tag{1a}$$

where

$$\eta \equiv \rho/\rho_o \tag{1b}$$

and

$$\nu \equiv 1 - \eta^{-\frac{1}{3}} \quad .$$

The quantity L represents the latent heat of vaporization for the solid and ρ_o is its density at zero pressure. The quantities b_r and b_a are undetermined parameters. The above expression was discarded and instead a modified Morse pressure expression (c.f. Eq. 4 in Ref. 1) was adopted.

In this work, Eq. 1 is used directly to obtain the cold (T = 0°K) pressure and Hugoniot curves using the Slater,[2] Dugdale-MacDonald,[3] and free-volume[4] relations for the Grüneisen coefficient.

The modified pressure function obtained from Eq. 1 is given by

$$P'_M(\eta) \equiv \eta^2 \rho_o \frac{dE'_M(\eta)}{d\eta}$$

$$= a\, \eta^{\frac{2}{3}} \left[\left(\eta e^{b_r \nu} - e^{b_a \nu} + \frac{b_r}{2} \left(\eta^{\frac{2}{3}} e^{b_r \nu} - e^{b_a} \right) \right) \right] \qquad (2a)$$

with

$$b_a = 1 + b_r/2 \qquad (2b)$$

and

$$a = \frac{2}{3} L \rho_o \quad . \qquad (2c)$$

This expression differs from that of Eq. 4 in Ref. 1 by the second term in the square brackets which increases the pressure above than given by the original expression. The relationship between b_a and b_r given by Eq. 2b is obtained from the requirement that the pressure vanish for $\eta = 1$.

In this section the quantities b_r and a will be treated as empirically determined parameters evaluated from the experimental value of the iso-

thermal bulk modulus and the high compression limit for the pressure of a Fermi-Dirac gas.

The isothermal bulk modulus is defined as

$$B \equiv \rho \left.\frac{dP}{d\rho}\right)_T = \eta \left.\frac{\partial P}{\partial \eta}\right)_T \quad . \tag{3}$$

Hence, we obtain, for T = 0 °K

$$B_o(\eta) = \frac{a}{3}\left\{ e^{b_r \nu}\left[5\eta^{\frac{5}{3}} + 3b_r\eta^{\frac{4}{3}} + \frac{b_r^2}{2}\ \eta\right] - e^{b_a \nu}\left[2b_a\eta^{\frac{2}{3}} + b_a^2\eta^{\frac{1}{3}}\right]\right\} \quad . \tag{4}$$

In the limit than $\eta \to 1$, we have

$$B_{oo} = \frac{a}{3}\left\{\left[3 + b_r - b_a\right] + \frac{b_r}{2}\left[2 + b_r - b_a\right]\right\} \tag{5a}$$

or using Eq. 2b,

$$B_{oo} = \frac{a}{3}\left\{2 + b_r + \frac{b_r^2}{4}\right\} \quad . \tag{5b}$$

This result differs from that of Ref. 1 by the addition of the second square bracket in Eq. 5a.

In the very high compression limit,

$$\lim_{\eta \to \infty} \nu = 1 \ ,$$

that is $\eta^{-\frac{1}{3}} << 1$, the modified pressure tends to the limit

$$\lim_{v \to \infty} P'_M(\eta) = a\eta^{\frac{5}{3}} e^{b_r} \quad . \tag{6}$$

In this limit the pressure due to a Fermi-Dirac gas is:

$$P_\infty = \frac{2}{3} C_f \left(\frac{Z}{A} N_o \rho_o\right)^{\frac{5}{3}} \eta^{\frac{5}{3}} \quad , \tag{7}$$

where $C_f = 3.5050 \times 10^{-27}$ erg-cm^2, N_o is Avogadro's number, Z is the atomic number, and A is the atomic weight.

Equating these two limiting expressions, we obtain an expression for the parameter a in terms of b_r. This, in conjunction with Eq. 5b yields,

$$B_{oo} = \frac{Ke^{-b_r}}{3} \left\{2 + b_r + \frac{b_r^2}{4}\right\} \tag{8a}$$

with

$$K \equiv \frac{2}{3} C_f \left(\frac{Z}{A} N_o \rho_o\right)^{\frac{5}{3}} \quad . \tag{8b}$$

Hence, given the values of ρ_o and B_{oo} from Table I of Ref. 1, we may obtain values of a and b_r for the eight metals studied. These values are summarized in Table 1.

With these parameters, Eq. 2 gives the zero temperature isotherm, the so-called cold compression curve, $P_c(\eta)$. The energy along this isotherm is given by

$$E_c(\eta) = \frac{1}{\rho_o} \int_1^\eta \frac{P_c(\eta')}{\eta'^2} d\eta' \quad . \tag{9}$$

This may be evaluated directly, using Eq. 2, to yield

$$E_c(\eta) = \frac{3}{2}\frac{a}{\rho_o}\left\{\eta^{\frac{2}{3}}\ e^{b_r\nu} - 2e^{b_a\nu} + 1\right\} \quad . \tag{10}$$

The pressure along the Hugoniot curve assuming a Mie-Grüneisen equation of state is given by:

$$P_H(\eta) = \frac{P_c(\eta) - \eta\rho_o\gamma(\eta)E_c(\eta)}{1 - (\eta - 1)\gamma(\eta)/2} \quad , \tag{11}$$

where $\gamma(\eta)$ is the Grüneisen coefficient. The three models for $\gamma(\eta)$ commonly used are the Slater,[2] Dugdale-MacDonald,[3] and free-volume theory.[4] These may be combined into a single expression[5]

$$\gamma_t(\eta) = \frac{t - 1}{3} + \frac{1}{2}\frac{N(\eta,t)}{D(\eta,t)} \tag{12a}$$

with

$$N(\eta, t) = \eta^2\ \frac{d^2P(\eta)}{d\eta^2} + \frac{2}{3}(1 - 2t)\ B(\eta) - \frac{2}{9}(1 + t)\ (1 - 2t)\ P(\eta) \tag{12b}$$

and

$$D(\eta, t) = B(\eta) - \frac{2}{3}(1 + t)\ P(\eta) \quad . \tag{12c}$$

The parameter t is used to select the particular model for the Grüneisen coefficient. That is,

$$t = \begin{cases} -1 \ ; \text{ Slater model} \\ \ \ 0 \ ; \text{ Dugdale-MacDonald model} \\ +1 \ ; \text{ free-volume model} \end{cases}$$

In the limit as $\eta \to 1$, the values of $\gamma(1)$ for the different models differ by 1/3 proceeding from the largest value at t = - 1 and going to the lowest at t = 1. A comparison of the values obtained from the Dugdale-MacDonald model in this work with those from Table II of Ref. 1, along with the experimental "lattice specific heat" values given there, are presented in Table II.

The Hugoniot and cold compression curves from Eqs. 2 and 11 are evaluated using the parameter values from Table I to yield Figs. 1 through 4. The cold compression curves have the label "c," whereas the Hugoniot curves using the various models for the Grüneisen coefficient are labeled with their appropriate value of t.

The figures contain some experimental information, referenced in an abbreviated form. A general feature of the Hugoniot results for these materials is that below compressions of approximately 1.4, the different Grüneisen coefficient models give essentially the same results. Above this value of η, the spread in the Hugoniots obtained for the different models becomes more pronounced.

The results produced by this method for Cu, Be, W, and Ni compared with those of Ref. 1 are of equivalent quality when compared with experimental data. As mentioned in Ref. 1, the results for Ti may not be expected to agree well with experiment because of a phase transition [α(hcp) $\to$ β(bcc) at 880 °C]. However, Ref. 1 produces results closer to those of experiment. For Mo, Ref. 1 produces the best comparison and for Pb, the current results are extremely poor in contrast to those of Ref. 1. The most striking improvement of the current results lies with the computation of the Al Hugoniot.

In general, those results which disagree with the experimental data do so by producing pressure curves which increase faster with compression than the data. This would imply that a smaller value of B_{oo} is necessary when determining the parameter b_r in order to improve agreement experiment. In order to fit the experimental data for Mo, W, and Pb in the compression range below 1.4, the values of B_{oo} could be empirically adjusted downward by 26%, 38%, and 35% respectively. However, in the case of Pb, even with this adjustment, the Hugoniots above compressions of 1.6 were still in large disagreement with the data (see Fig. 5). Since values of ρ_o and B_{oo} were taken as those given at standard conditions (1 atm pressure, and ~ 300°K) some adjustment might be warranted. However 25-40% may be to large to be considered realistic.

PARAMETERS FOR MODIFIED MORSE POTENTIAL FROM COHESIVE ENERGY DATA

From work with the Modified Morse Potential, we have a constant a to be evaluated.

$$a = \frac{2}{3} L \rho_o \quad , \tag{13}$$

where ρ_o is the density at T = 0 and P = 0 atmospheres and L is the cohesive energy. In that work "a" is obtained by fitting the isothermal compressibility to experiment and assuming that the pressure goes to the limit of a free electron gas at high compressions. In this regard, the value of L is never needed.

From Brewer's work[9] we are given $\mathcal{L} = L \times A_w$, where A_w = atomic weight. Then

$$a = \frac{2}{3} \frac{\mathcal{L}}{A} \rho_o \quad . \tag{14}$$

Using Brewer's values of $\mathcal{L}$ and data from the CRC Handbook for ρ_o and A_w, we obtain values for the parameter a. These are presented along with a comparison with those obtained using the Thomas-Fermi limit (labeled FE) in Table III.

Since the equation for b_r is a quadratic, there are two solutions. Of this pair of numbers, only the solution with the positive sign is physically acceptable. These pairs of solutions are shown in Table IV.

Figures 5 through 8 show the cold pressure curves and sets of Hugoniots using the new values of a and b_r. Experimental data shown on these figures are the same as those given in Figures 1 through 4.

By comparing the results in equivalent figures, the overall quality of agreement improves using the prescription of cohesive energies with the exception of Cu and Mo. The results for Pb are greatly improved.

TABLE I

PHYSICAL PROPERTIES AND PRESSURE PARAMETERS

Element	ρ_o(gm/cm^3)	B_{oo}(Mbar)	a(Mbar)	b_r
Be	1.8450	1.14	0.491	2.88
Al	2.7847	0.763	0.205	4.382
Ti	4.5065	1.07	0.249	4.91
Ni	8.8968	1.90	0.355	5.75
Cu	8.9206	1.37	0.236	6.09
Mo	10.2041	2.69	0.549	5.40
W	19.1571	3.08	0.494	6.415
Pb	11.3379	0.447	0.0545	7.717

TABLE II

GRÜNEISEN COEFFICIENTS FOR DUGDALE-MACDONALD MODEL

Element	γ(this work)	γ(Ref. 1)	γ(exp)
Be	1.443	1.09	1.30
Al	1.768	1.35	2.21
Ti	1.887	1.36	1.35
Ni	2.079	2.10	2.00
Cu	2.158	2.22	2.01
Mo	1.999	1.44	1.62
W	2.234	1.81	1.69
Pb	2.542	2.15	2.77

TABLE III

PRESSURE PARAMETERS FROM COHESIVE ENERGIES

$$a = \frac{2}{3} \frac{\mathcal{L}}{A_w v_o} 0.04184 \quad \text{(Mbars)}, \quad [\mathcal{L} \text{ is in kcal/mole}].$$

Element	a(Mbars)	a/a(FE)	b_r	$b_r/b_r(FE)$
Be	0.43758	0.891	3.22138	1.119
Al	0.22484	1.097	4.05989	0.926
Ti	0.29552	1.187	4.28083	0.872
Ni	0.43322	1.220	4.97346	0.865
Cu	0.31623	1.340	4.92730	0.809
Mo	0.46732	0.851	6.06689	1.123
W	0.60101	1.217	5.58264	0.870
Pb	0.07149	1.312	6.42802	0.833
Fe	0.38634	0.673	6.66670	1.328

TABLE IV

COMPUTATION OF b_r

$$Bo = \frac{a}{12}\left[8 + 4\,b_r + b_r^2\right]$$

$$b_r^2 + 4b_r + \left(8 - \frac{12\,B_o}{a}\right) = 0 = b_r^2 + 4b_r + \text{"C"}$$

	"C"	b_{r_1}	b_{r_2}
Be	- 23.26285	- 7.22138	3.22138
Al	- 32.72229	- 8.05989	4.05989
Ti	- 35.44884	- 8.28083	4.28083
Ni	- 44.62915	- 8.97376	4.97346
Cu	- 43.98748	- 8.92730	4.92730
Mo	- 61.07472	- 10.06689	6.06689
W	- 53.49648	- 9.58264	5.58264
Pb	- 67.03147	- 10.42802	6.42802

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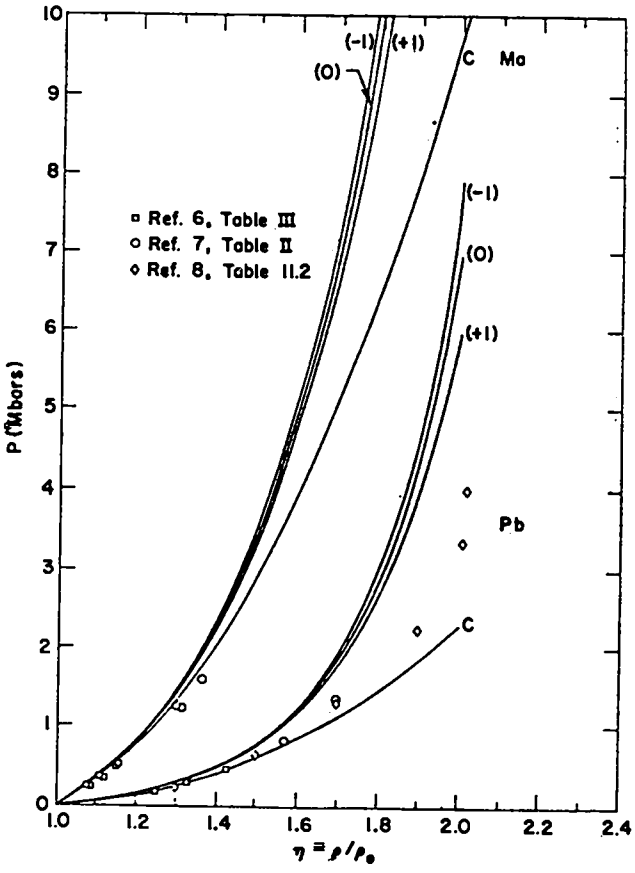
P (Mbars)
η = ρ/ρ₀
(-1)
(+1)
(0)
C
Mo
Ref. 6, Table III
Ref. 7, Table II
Ref. 8, Table II.2
(-1)
(0)
(+1)
Pb
C
θ

Fig. 1.

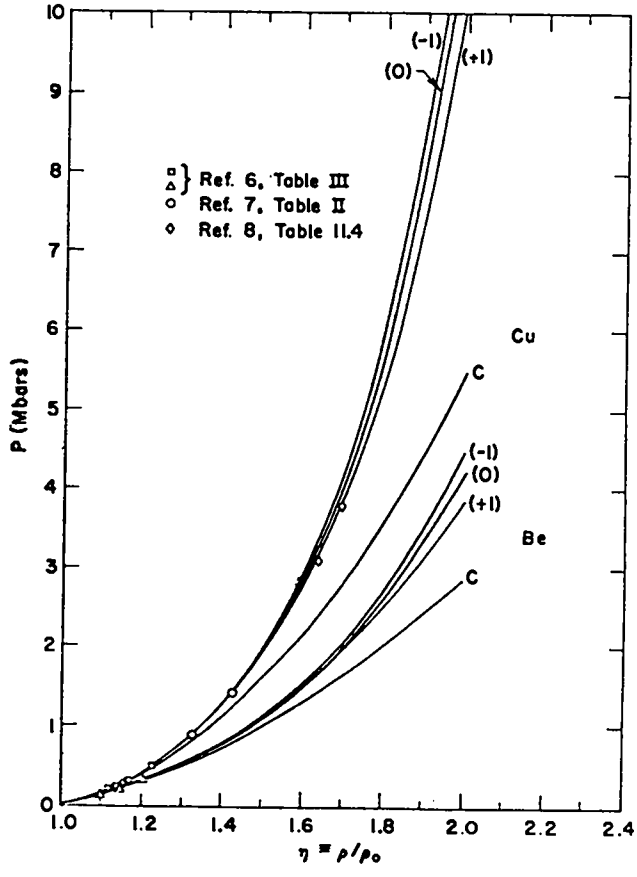
P (Mbars)
η = ρ/ρ₀
(-1)
(+1)
(0)
Ref. 6, Table III
Ref. 7, Table II
Ref. 8, Table II.4
Cu
C
(-1)
(0)
(+1)
Be
C

Fig. 2.

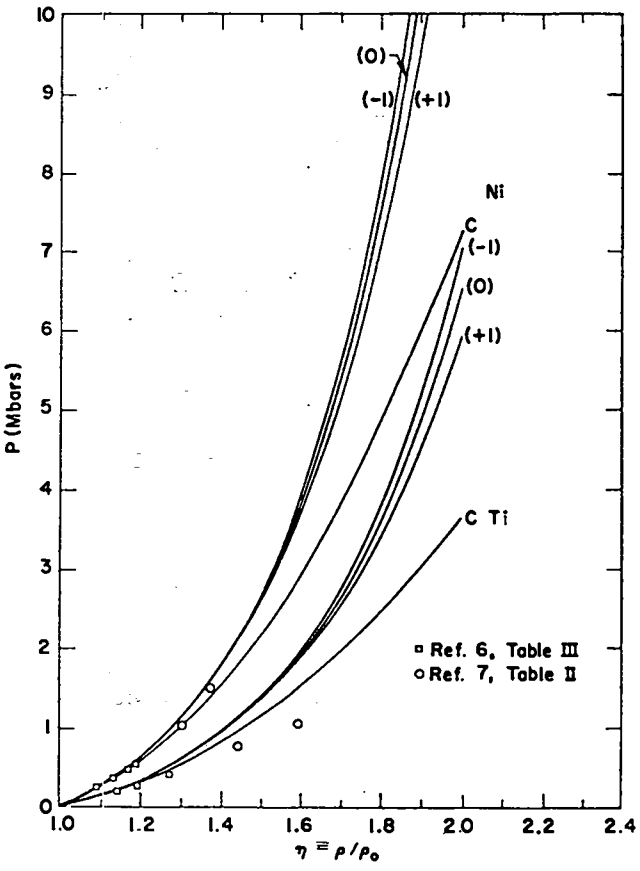

Fig. 3.

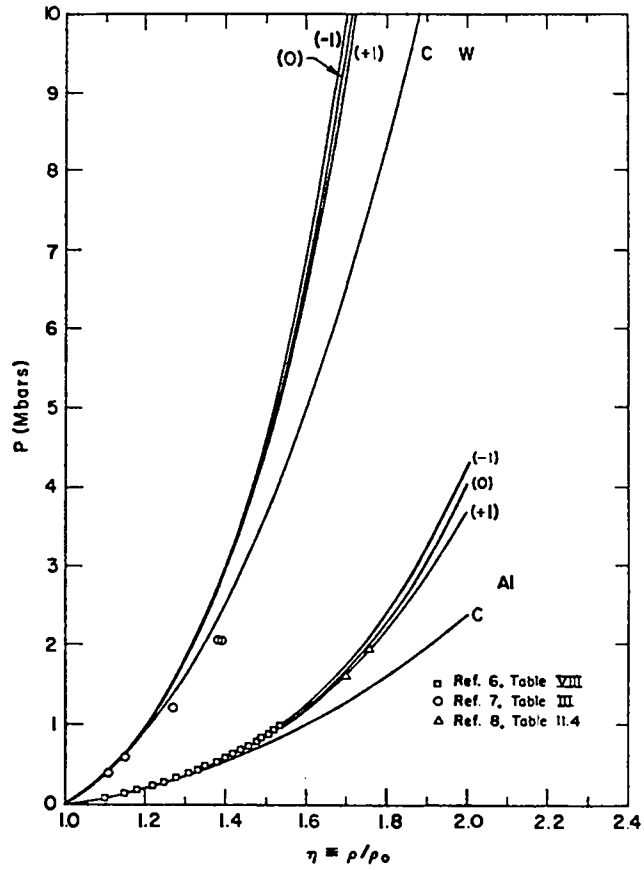

Fig. 4.

Figures 1 through 4 display the zero temperature isotherms and Hugoniots for two materials. The isotherms were obtained using the Fermi-Dirac electron gas limit for determining the parameter "a."

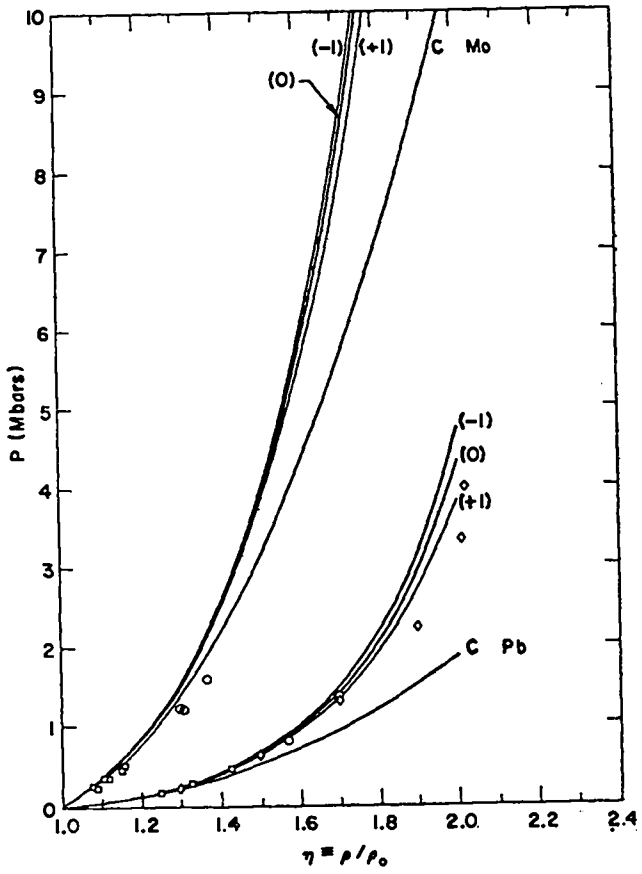
(-1)
(+1)
C Mo
(0)
(-1)
(0)
(+1)
C Pb
P (Mbars)
η = ρ/ρ₀

Fig. 5.

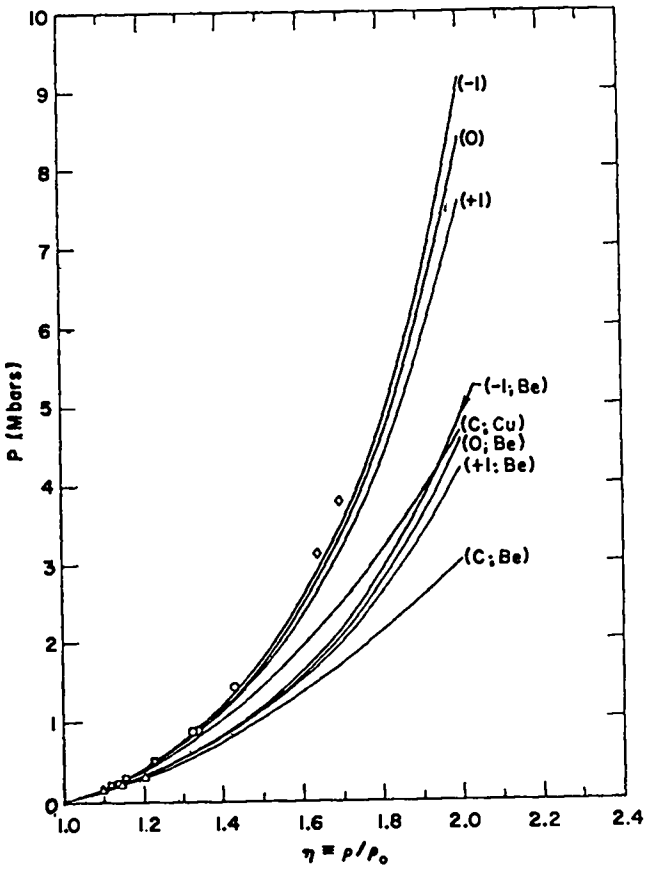
(-1)
(0)
(+1)
(-1; Be)
(C; Cu)
(O; Be)
(+1; Be)
(C; Be)
P (Mbars)
η = ρ/ρ₀

Fig. 6.

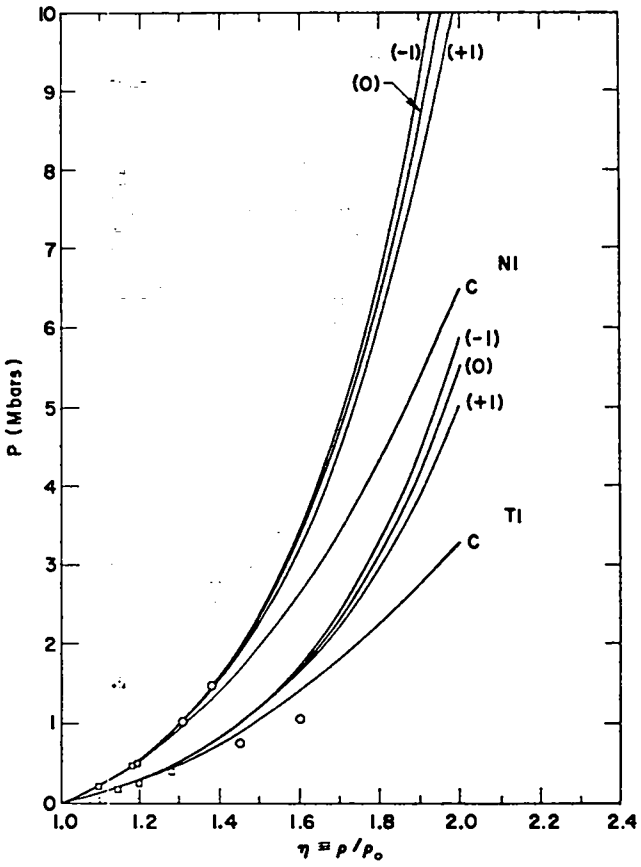

Fig. 7.

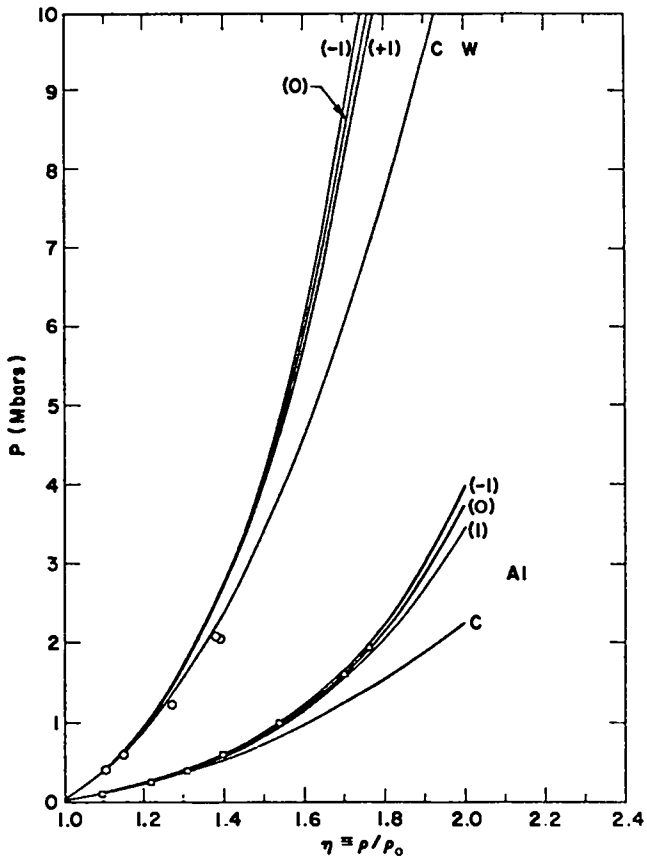

Fig. 8.

Figures 5 through 8 show the equivalent information as the first four figures, but with the isotherm parameter "a" obtained from Brewer's cohesive energies. The experimental data shown in these figures are the same as those referenced in Figures 1 through 4.

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