International Journal of Thermophysics, Vol. 9, No. 6, 1988

The Tait Equation: 100 Years On[1]

J. H. Dymond[2] and R. Malhotra[3]

The "Tait equation," which is now widely used to fit liquid density data over wide pressure ranges, is a modification of the original equation of Tait, published 100 years ago, to fit his results on the compressibility of fresh water and seawater at different pressures. The range of applicability of these different equations is discussed and it is concluded that their simplicity and accuracy in reproducing high pressure density data for dense gases, liquids, solids, and liquid mixtures will ensure their continued use.

KEY WORDS: density; high pressure; Tait equation.

1. INTRODUCTION

Isothermal density data for liquids up to elevated pressures are widely represented [1–8] by the following equation:

$$\frac{\rho-\rho_0}{\rho}=C\log[(B+p)/(B+p_0)] \tag{1}$$

or the equivalent expression in terms of volume

$$\frac{v_0-v}{v_0}=C\log[(B+p)/(B+p_0)] \tag{2}$$

where the subscript o refers to the low-pressure, usually 0.1 MPa or saturation pressure, value and B and C are parameters derived from the fit.

---

[1] Paper presented at the Tenth Symposium on Thermophysical Properties, June 20–23, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom.

[3] Atomic and Molecular Physics Laboratories, Research School of Physical Sciences, The Australian National University, Canberra ACT 2600, Australia.

This equation, frequently referred to as the Tait equation, very satisfactorily reproduces liquid density measurements over a wide pressure range.

Indeed, Le Neindre and Tufeu [9] considered it to be the most satisfactory of the equations they investigated. However, the interesting fact is that, as far as we know, this equation was not proposed by Tait or ever used by him.

In this paper, a brief historical background is given, leading to the true Tait equation [10] with examples of its application. Then an account of the derivation of the above equation—the modified Tait equation—is outlined, and examples are given of its application to density data for liquids and liquid mixtures.

2. THE TRUE TAIT EQUATION

The experimental investigations of the compressibility of glass, mercury, fresh water, and seawater which led to the true Tait equation for compressibility of liquids [10] were carried out by the noted Scottish mathematician and physicist Peter Guthrie Tait following the scientific expedition of H.M.S. Challenger from 1873 to 1876 (Fig. 1). A major

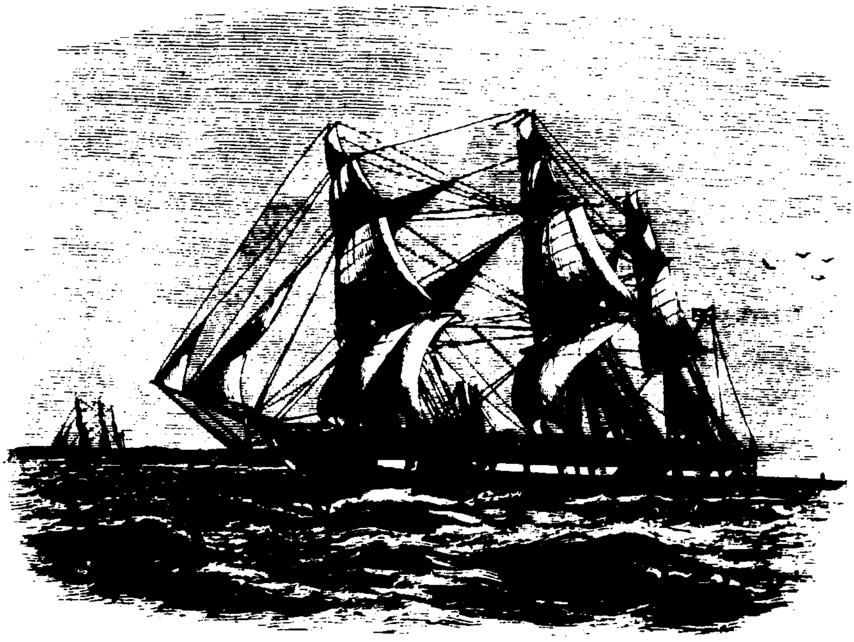

Fig. 1. H.M.S. Challenger.

objective of this expedition, as stated in the report of the committee set up by the Royal Society (London) dated November 30, 1871, was

> 1. To investigate the Physical Conditions of the Deep Sea, in the great Ocean-basins,—the North and South Atlantic, the North and South Pacific, and the Southern Ocean (as far as the neighbourhood of the great ice-barrier); in regard to Depth, Temperature, Circulation, Specific Gravity, and Penetration of Light; the observations and experiments upon all these points being made at various ranges of depth from the surface to the bottom.

With regard to the temperature measurement using self-registering thermometers, there was uncertainty concerning the corrections to be applied for elevated pressure on the instruments, and Tait, who was Professor of Natural Philosophy at the University of Edinburgh, was asked to investigate. He showed that the surprisingly large effects that had previously been found in direct experiments in pressure vessels with thermometers with protected bulbs arose from heat due to compression of the vulcanite on which the thermometers were mounted. Circumstances in the pressure cylinder differed considerably from when the thermometers were let down in the sea, where heat due to compression developed very slowly and was removed by convection. In fact, as Tait found, it was scarcely necessary to apply corrections for pressure.

With the apparatus which he constructed, Tait determined the compressibility of fresh water and seawater at different temperatures. From his results, he wrote [10],

> I easily found that the average compressibility for two tons pressure (at any one temperature) is somewhat less than half the sum of those for 1 and for 3 tons. Thus the average compressibility through any range of pressure falls off more and more slowly as that range is greater. And, within the limits of my experiments, I found that this relation between pressure and average compressibility could be fairly well represented by a portion of a rectangular hyperbola, with asymptotes coincident with and perpendicular to the axis of pressure. Hence at any one temperature (within the range I was enabled to work in), if v_0 be the volume of fresh water at one atmosphere, v that under an additional pressure p, we have
>
> $$\frac{v_0 - v}{p v_0} = \frac{A}{\pi + p}$$
>
> very nearly, A and π being quantities to be found.

In 1967, Hayward [11] made a comparative study of compressibility equations. As he stated, "why Tait chose to express it in this form and then laboriously to fit his experimental points to a hyperbola, when he could have inverted the equation and fitted his points to a straight line, will

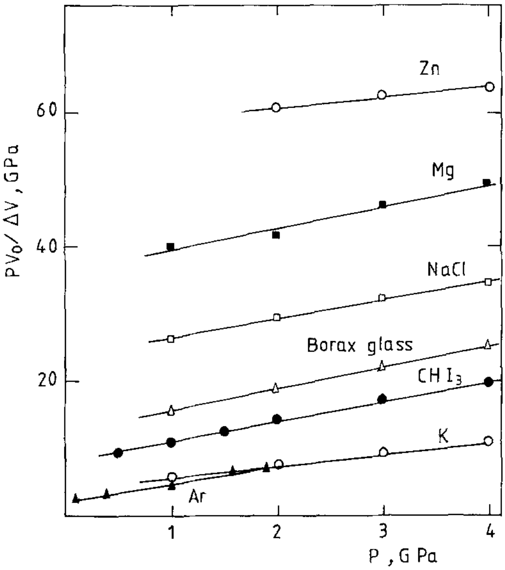

Fig. 2. Pressure dependence of the isothermal secant bulk modulus for different solids.

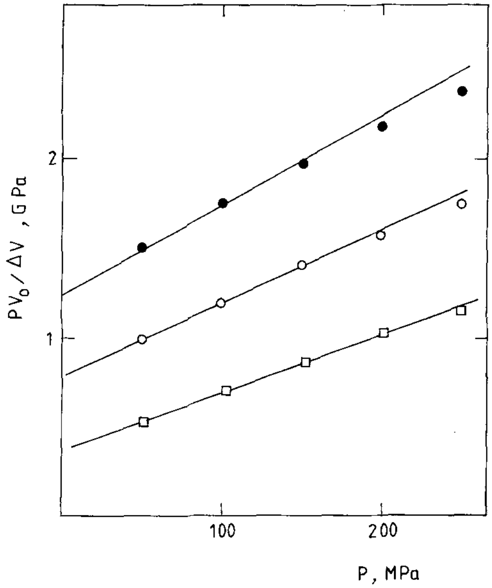

Fig. 3. Pressure dependence of the isothermal secant bulk modulus for hydrocarbons. (□) *n*-Hexane at 373 K [15]; (○) *n*-heptane at 303 K [16]; (●) mesitylene at 298 K [17].

always remain a mystery." As he pointed out, the equation then becomes the linear pressure equation for the isothermal secant bulk modulus:

$$\frac{pv_0}{v_0 - v} = \frac{\pi}{A} + \frac{p}{A} \tag{3}$$

In this form, the Tait equation very satisfactorily represents the experimental compressibility data for solids [12–14] up to a few gigapascals of pressure. This is illustrated in Fig. 2 for rare-gas solids, metals, inorganic and organic solids, and glasses. Similar slopes were observed [12] for similar groups of materials.

For liquids, the linear secant bulk modulus equation fits the experimental measurements within the estimated uncertainty over a more limited pressure range. In the case of organic liquids, as shown in Fig. 3 using accurate density values for *n*-hexane [15], *n*-heptane [16], and mesitylene [17], the linear pressure dependence of the secant bulk modulus extends only to just above 150 MPa. For water, a linear relationship between secant bulk modulus and pressure exists up to 300 MPa.

3. THE MODIFIED TAIT EQUATION

The earliest occurrence of the modified Tait equation, Eq. (1) or (2), appears to be in a paper by Tammann [18]. The equation which he attributed to Tait was obtained by replacing Tait's average compressibility with the corresponding differential coefficient. Thus Tammann wrote

$$\frac{\Delta v}{\Delta p} = \frac{A}{B + p} \tag{4}$$

This, when inverted, corresponds to the linear mixed-modulus equation.

As Tammann showed, Eq. (4) can be integrated to give

$$v = v_0[1 - A \ln(B + p)/B] \tag{5}$$

which on rearrangement, replacement of A by C and inclusion of p_0, gives Eq. (2).

Hayward [11] considered that this equation had no advantages over the linear secant bulk modulus equation, pointing out that it did not fit the experimental data for water nearly so well as Eq. (3). However, the modified Tait equation has become widely accepted as the equation to use to represent high-pressure density data for liquids and liquid mixtures, especially for pressures extending to above 150 MPa, where deviations from the linear pressure dependence of the secant bulk modulus become apparent.

From measurements on hydrocarbons, it appeared [3, 19] that C was temperature independent but B decreased with increases in temperature. The values reported for C were found to be constant for a given series; for example, Eduljee et al. [19] obtained $C = 0.2172$ for n-alkanes and Cutler et al. [3] gave 0.2058 for C for aliphatic hydrocarbons. Although these values are in reasonable agreement, the number of figures given implies a significant difference in C for different groups of compounds. However, where the measurements extend to pressures of 150 to 200 MPa, there is a possible variation of about 0.02 in C which, with a corresponding change in B, will allow an equally satisfactory fit to the density data for n-alkanes. Where the pressure range extends to 500 MPa, the flexibility in C is greatly reduced. For a systematic investigation of the applicability of the modified Tait equation, high-pressure density measurements are required for several members of homologous series, and in recent years accurate measurements have been made [8, 15] for liquid n-alkanes at pressures up to 500 MPa from 25 to 100°C to supplement the older values. In a recent paper [20], attention was restricted to the industrially more useful pressure range up to 150 MPa, where it was found for n-alkanes that C could be taken as 0.2000. The optimized B values lay on smooth curves when plotted versus reduced temperature, the curves being simply displaced from one another.

For temperatures below 0.66 times the critical temperature, B was given by an equation in reduced temperature, T_r, where temperature is divided by critical temperature, adjusted for the hydrocarbon number, C_n:

$$B = a_0 + a_1 T_r + a_2 T_r^2 - (C_n - 6) \tag{6}$$

This was shown to give a very satisfactory correlation of all the n-alkane density data and to be readily extended to mixture densities. Parameter C was taken as the mole fraction average of the values for the pure components, and the critical temperature for the mixture taken as the value for an n-alkane with a corresponding carbon number. Densities for 22 binary mixtures and 1 ternary n-alkane mixture were very satisfactorily reproduced by this method.

Since then we have considered aromatic hydrocarbons for which accurate densities are available up to elevated pressures [8, 21–24], for temperatures up to 0.66 times the critical temperature. Here it is found that C needs to be higher, about 0.216, to give the optimum data fit. The B values corresponding to $C = 0.216$ decrease with increases in temperature, as shown in Fig. 4. The vertical lines indicate the possible variation in B which will still give a density fit to within 0.2% at the experimental pressures. The solid line can be represented by Eq. (6), with $a_0 = 494$, $a_1 = -1110$, and $a_2 = 672$, without the final term. It remains to be seen

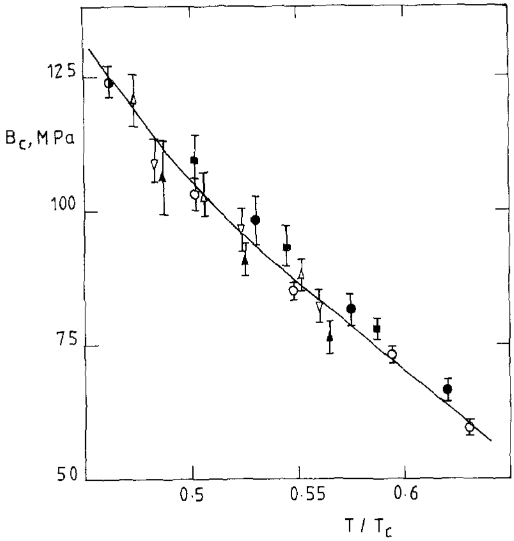

Fig. 4. Plot of B_c versus reduced temperature T_r for aromatic hydrocarbons. Solid line represents $B+(C_n-6)$, Eq. (6), with values for the coefficients given in the text: (●) benzene; (○) toluene; (△) *o*-xylene; (▽) *m*-xylene; (▲) *p*-xylene; (■) ethyl benzene.

Table I. Temperature-Independent *C* Values for Liquids

Compound	*T* (K)	P_{max} (MPa)	*C*	Ref. No.
Cyclohexane	298–348	100	0.1988	5
	303–393	250	0.2095	25
Chlorobenzene	298–358	100	0.2159	26
Bromobenzene	298–358	100	0.2159	26
Nitrobenzene	298–358	100	0.2159	26
Aniline	298–358	100	0.2159	26
1-Chlorobutane	303	500	0.173	27
1, 2-Dichloroethane	298–398	101	0.232	28
Tetrachloroethane	298	100	0.2126	2
Acetone	298	100	0.2356	2
Diethyl ether	273–353	100	0.207	29
Ethyl acetate	253–313	150	0.202	30
Glycerol	223–353	280	0.2568	6
Pentan-1, 5-diol	253–308	280	0.3146	6
Polyisobutylene	326–383	100	0.2006	31
Poly(vinyl acetate)	337–393	100	0.2409	31

whether a common value for C for both *n*-alkanes and aromatic hydrocarbons is possible.

There is evidence that for liquids in general C is not a constant. Examples of this are given in Table I, where C ranges from 0.173 for 1-chlorobutane [27] to >0.25 for compounds containing several hydroxyl groups [6]. As mentioned above, there is some flexibility in C where the density measurements extend only to 100 MPa and the difference in the values reported for cyclohexane [5, 25] corresponds with that found for *n*-alkanes. It is worthy of note that C for liquid polymers falls in the range of values found for simple (nonassociated) liquids.

For water C is found to vary strongly with changes in temperature [32], as given in Table II. It appears that a temperature-dependent C is sometimes necessary when density data extend to low temperatures [33, 34] or where measurements of higher accuracy are available [7]. In each case, C is found to increase with increases in temperature (Table II).

With regard to parameter B, values decrease with increases in temperature and this temperature dependence has been variously reported as a linear variation with reciprocal temperature [30], a linear decrease with temperature [35], and a quadratic expression in temperature difference from some reference temperature [3]. Experimental density measurements cover an insufficient temperature range to determine the complete curve but Ginell [36], using helium densities, suggests that B passes through a maximum at low temperatures and then decreases to a negative number, equal to the negative of the critical pressure at the critical temperature.

For mixtures, the modified Tait equation gives a good fit to experimental densities up to elevated pressure. The C values generally vary fairly smoothly with composition, as reported for benzene + chlorobenzene, and + bromobenzene [4], + nitrobenzene [37], + toluene and + *o*-xylene [38], and + cyclohexane [5]. This is not the case where hydrogen bonding

Table II. Temperature-Dependent C Values for Liquids

Compound	T (K)	$P_{\max}$ (MPa)	C	Ref. No.
Water	283	200	0.2691	32
	348	200	0.3467	32
Bromobutane	203	550	0.2176	33
	373	550	0.2648	33
Acetonitrile	253	300	0.194	34
	313	300	0.24	34
Bromobenzene	278	200	0.2209	7
	323	275	0.2251	7

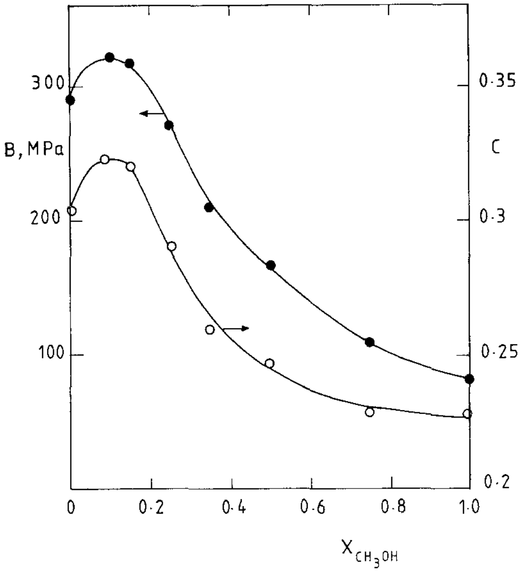

Fig. 5. Composition dependence for parameters C and B for methanol + water at 298 K.

effects occur, as shown in Fig. 5 for methanol + water [32] at 298 K. The variation in C with composition is matched closely by the composition dependence of B. Similar behavior has been found [39] for the composition dependence of B and C derived from density data at 298 K at pressures up to 150 MPa for water + propanol (maximum at 0.05 mole fraction of propanol), water + acetone (maximum at 0.1 mole fraction of acetone), and water + dimethyl sulfoxide (maximum at about 0.25 mole fraction of dimethyl sulfoxide). Interestingly, for aqueous solutions of inorganic salts, it has been found [40] that for pressures up to 100 MPa at temperatures from 298 to 358 K, C can be taken as equal to the value derived for water.

As a result of this review, it is apparent that much further work is required to give uncertainty limits on C and B values derived from density measurements for different systems in order to determine the specific dependence of these parameters on temperature and, for mixtures, on composition.

4. CONCLUSIONS

The original Tait equation in its inverted form gives an excellent representation of density data for solids at pressures up to a few gigapascals and for organic liquids generally up to 150 or 200 MPa. For density measurements for liquids and liquid mixtures up to higher pressures, the modified Tait equation gives a greatly improved fit. Although these equations have their origin in the paper of Tait published 100 years ago, their simplicity and accuracy in reproducing experimental densities will ensure their continued use well into the future.

REFERENCES

1. R. E. Gibson and O. H. Loeffler, *J. Phys. Chem.* **43**:207 (1939).
2. D. M. Newitt and K. E. Weale, *J. Chem. Soc. (Lond.)* 3092 (1951).
3. W. G. Cutler, R. H. McMickle, W. Webb, and R. W. Schiessler, *J. Chem. Phys.* **29**:727 (1958).
4. T. Takagi and H. Teranishi, *J. Chem. Thermodyn.* **14**:577 (1982).
5. H. Kashiwagi, T. Fukunaga, Y. Tanaka, H. Kubota, and T. Makita, *Rev. Phys. Chem. Jap.* **49**:70 (1979).
6. G. E. McDuffie, J. W. Forbes, W. M. Madigosky, and J. J. Von Bretzel, *J. Chem. Eng. Data* **14**:176 (1969).
7. A. J. Easteal and L. A. Woolf, *Int. J. Thermophys.* **8**:557 (1987).
8. J. H. Dymond, R. Malhotra, J. D. Isdale, and N. F. Glen, *J. Chem. Thermodyn.* **20**:603 (1988).
9. B. Le Neindre and R. Tufeu, *Proc. Int. CODATA Conf., Kyoto* (1981), p. 411.
10. P. G. Tait, *Physics and Chemistry of the Voyage of H.M.S. Challenger, Vol. 2, Part 4* (HMSO, London, 1888).
11. A. T. J. Hayward, *J. Appl. Phys.* **18**:965 (1967).
12. P. R. Couchman and C. L. Reynolds, Jr., *J. Appl. Phys.* **47**:5201 (1976).
13. J. W. Stewart, *Phys. Chem. Solids* **1**:146 (1956).
14. *American Institute of Physics Handbook* (McGraw–Hill, New York, 1972), pp. 4–38.
15. J. H. Dymond, K. J. Young, and J. D. Isdale, *J. Chem. Thermodyn.* **11**:887 (1979).
16. A. K. Doolittle, *J. Chem. Eng. Data* **9**:275 (1964).
17. P. W. Bridgman, *Proc. Am. Acad. Arts Sci.* **77**:129 (1949).
18. G. Tammann, *Z. Phys. Chem.* **17**:620 (1895).
19. H. E. Eduljee, D. M. Newitt, and K. E. Weale, *J. Chem. Soc. (Lond.)* 3086 (1951).
20. J. H. Dymond and R. Malhotra, *Int. J. Thermophys.* **8**:541 (1987).
21. M. J. P. Muringer, N. J. Trappeniers, and S. N. Biswas, *Phys. Chem. Liq.* **14**:273 (1985).
22. H. Kashiwagi, T. Hashimoto, Y. Tanaka, H. Kubota, and T. Makita, *Int. J. Thermophys.* **3**:201 (1982).
23. J. H. Dymond, N. Glen, J. Robertson, and J. D. Isdale, *J. Chem. Thermodyn.* **14**:1149 (1982).
24. T. Makita, Personal communication.
25. A. Z. Golik, I. I. Adamenko, and V. V. Borovik, *Ukr. Fiz. Zh.* **7**:2075 (1975).
26. R. E. Gibson and O. H. Loeffler, *J. Am. Chem. Soc.* **61**:2515 (1939).
27. J. F. Skinner, E. L. Cussler, and R. M. Fuoss, *J. Phys. Chem.* **72**:1057 (1968).
28. A. Kumagai and S. Takahashi, *J. Chem. Thermodyn.* **17**:977 (1985).
29. A. Wohl, *Z. Phys. Chem.* **99**:234 (1921).
30. A. Kumagai and H. Iwasaki, *J. Chem. Eng. Data* **24**:261 (1979).
31. S. Beret and J. M. Prausnitz, *Macromol.* **8**:536 (1975).
32. H. Kubota, S. Tsuda, M. Murata, T. Yamamoto, Y. Tanaka, and T. Makita, *Rev. Phys. Chem Jap.* **49**:59 (1979).

33. M. Millet and G. Jenner, *High Temp. High Press.* **1**:697 (1969).
34. R. Landau and A. Wurflinger, *Ber. Bunsenges. Phys. Chem.* **84**:895 (1980).
35. H. Carl, *Z. Phys. Chem.* **101**:238 (1922).
36. R. Ginell, *J. Chem. Phys.* **35**:1776 (1961).
37. T. Takagi and H. Teranishi, *J. Chem. Thermodyn.* **14**:1167 (1982).
38. T. Takagi, *Rev. Phys. Chem. Jap.* **48**:17 (1978).
39. T. Moriyoshi and Y. Uosaki, *Aairo Shiken* **33**:127 (1984).
40. R. E. Gibson and O. H. Loeffler, *Ann. N.Y. Acad. Sci.* **51**:727 (1949).