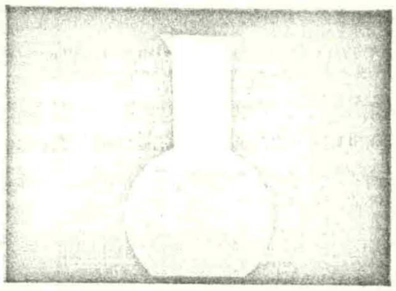
Chem. Eng. (N.Y.), 76, 14, 129-31 (1969)

Estimating Thermophysical Properties of Liquids



Part 9—Compressibility, Velocity of Sound

Rough engineering estimates of isothermal and adiabatic compressibilities and velocity of sound can be obtained with the not-too-reliable techniques available.

PHILLIP I. GOLD, California State College at Los Angeles, and GILBERT J. OGLE, TRW Systems*

We continue our series on the estimation of thermophysical properties of liquids with a consideration of three closely related and useful properties: isothermal and adiabatic compressibilities (α_T and α_a, respectively), and the velocity of sound u.

The techniques evaluated here for the calculation of these properties are relatively simple and yield rough engineering estimates. However, caution should be exercised so that an unwarranted degree of reliability will not be ascribed to the results.

* To meet the authors, see Chem. Eng., Oct. 7, 1968, p. 154.

Nomenclature

A, B, C	Constants
c_p	Heat capacity at constant pressure, cal./(g.-mole) (°K.)
c_v	Heat capacity at constant volume, cal./(g.-mole) (°K.)
M	Molecular weight
p^*	Vapor pressure, atm.
T	Temperature, °K.
T_c	Critical temperature, °K.
T_r	Reduced temperature, $T_r = T/T_c$
u	Velocity of sound, cm./sec.
V	Molar volume, cc./(g.-mole)
Z	Compressibility factor, dimensionless
α_a	Adiabatic compressibility, sq.cm./dyne
α_T	Isothermal compressibility, sq.cm./dyne
β	Constant
λ	Latent heat of vaporization, cal./g.
ρ	Density, g./cc.
σ	Surface tension, dynes/cm.

Thermodynamically, the three properties are defined, respectively, as:

$$\alpha_T = -(1/V)\,(\partial V/\partial P)_T \quad (1)$$

$$\alpha_a = -(1/V)\,(\partial V/\partial P)_s \quad (2)$$

$$u = (\partial P/\partial \rho)_s^{1/2} \quad (3)$$

where the subscript s refers to an isentropic process.

The first two equations represent exact thermodynamic definitions. The definition of the velocity of sound (Eq. 3), however, is subject to certain restrictions such as the assumption of small pressure and density differences across the sound wave. In addition, it must be assumed that the change in state of the fluid across the wave front (resulting from such factors as the pressure and density differences just mentioned) is essentially adiabatic, and that—if there is no internal friction or viscosity factor—the process is also reversible and, therefore, isentropic.

One very interesting aspect of the compressibilities is the relationship of the compressibility ratio, α_T/α_a, to the more familiar specific-heat ratio. It is not difficult to show that:

$$C_p/C_v = (\partial P/\partial V)_s/(\partial P/\partial V)_T = \alpha_T/\alpha_a \quad (4)$$

Combining Eq. (2) and (3):

$$\alpha_a = V/u^2, \text{ and} \quad (5)$$

$$C_p/C_v = \alpha_T u^2/V \quad (6)$$

Further manipulation of these equations yields other useful relationships between these values.

Methods for predicting isothermal and adiabatic compressibilities and velocity of sound—Table I

Parameter	Method	Reference
Isothermal compressibilty, α_T	Rao-Li	4
	Wada	12
Adiabatic compressibility, α_a	Rao	2
	Wada	12
Velocity of sound, u	Rao	3,5,8,9
	Rykov	6
	Surface tension	7

Predictive equations for isothermal and adiabatic compressibilities and velocity of sound—Table II

Parameter	Method	Equation
Isothermal compressibility, α_T	Rao-Li	$\alpha_T = [p^*Z(6 \ln Z - 11) \times (1.01325 \times 10^6)]^{-1}$ where $Z = \frac{82.06T}{p^*V}$.
	Wada	$\alpha_T = (M/\rho B)^7$ where B is a constant determined by the sum of the bond contributions given in Table III.
Adiabatic compressibility, α_a	Rao	$(1/\rho\alpha_a)^{1/2} = C(T_c - T)$ where C is a constant determined by one value of α_a and ρ.
	Wada	$\alpha_a = (M/\rho A)^7$ where A is a constant determined by the sum of the bond contributions given in Table III.
Velocity of sound, μ	Rao	$u = 0.032808(\beta\rho/M)^3$ where β is a constant determined by the sum of the structural contributions in Table IV.
	Rykov	$u = \left[\frac{c_p\lambda}{\alpha_T T(c_p - \alpha_T\lambda M)}\right]^{1/2} \times (3.2808)$ where c_p, λ and α_T are taken at absolute temperature T.
	Surface tension	$u = (355)(0.032808) \times \left[\frac{\sigma V^{2/3}}{MT_r}\right]^{1/2}$ where σ and V are taken at absolute temperature T.

Bond contributions for isothermal and adiabatic compressibilities (Wada's method)—Table III

Bond	Constant A	Constant B
C—C	−1.10	1.07
C—O	2.05	2.78
C—S	5.43	—
C—N	0.40	0.24
C—H	5.10	4.16
C—F	—	6.57
C—Cl	12.91	12.55
C—Br	15.54	15.33
C—I	19.65	—
O—H	4.64	5.07
N—H	5.57	5.00
C═C	5.68	6.36
C═O	9.93	9.08
C═S	16.83	—
C═N	7.60	—
N═O	8.17	8.28
C≡N	14.13	—
Ring	4.80	−0.43

Information regarding the velocity of sound is important in a variety of hydrodynamic calculations. Similarly, compressibility data can be useful for the extrapolation of saturated-liquid* densities to higher pressures.

Predictive Methods

The predictive methods evaluated here and their corresponding equations are listed in Tables I and II, respectively. Tables III and IV list the additive structural and bond contributions required in several of the procedures.

Results of Analysis, Recommendations

Table V summarizes the results of the statistical analysis of the methods evaluated. (The class symbols of Table V are defined in Part 8, Table IV, *Chem. Eng.*, May 19, 1969, p. 194.) Our analysis of the methods for the three properties showed this:

Isothermal Compressibility—Clearly, large uncertainties exist in the Rao-Li and Wada methods for predicting this property. The problem is further complicated by the small number of samples. A choice between the two methods is largely based on simplicity, available data and general applicability. The Wada method is simpler, requires less data, but is also not as widely applicable as the Rao-Li method.

Adiabatic Compressibility—Here, Rao's technique is recommended (calculations made on 146 organics yielded 95% reliability limits of ±7%), but the method does require at least one known value of adiabatic compressibility. Wada's method, on the

* Liquids at their saturation pressure as opposed to compressed liquids (liquids at higher pressures).

Structural contributions for calculating velocity of sound by Rao's method—Table IV

Types of Compounds	Constant β
Basic structure:	
Methane	1,850
Benzene	4,534
Cyclohexane	5,363
Naphthalene	6,566
Substituted radicals:	
>C<, >CH–, –CH₂–, –CH₃	872
–COO–	1,220
–C(=O)–H	449
–C(=O)–	872
>NH	638
–NH₂	478
–COOH	942
–C≡N	819
–O–	273
–OH	137
–Cl	610
–Br	692
–I	893
–NO₂	893
–S	550
=S	550
Double bonds	−254
Triple bonds	−507
Position contributions:	
Ortho	0
Meta	59
Para	117

ther hand, can be used even if no data are available.*

Velocity of Sound—Of the three methods considered for the velocity of sound, Rao's is the easiest to use, requires only density data, and appears to be the most reliable. Calculations on 144 organics yielded 95% reliability limits of ±23%. ■

* In this series, reliability limits means that 95% of the time the value calculated for *j*th thermophysical property by the *k*th method, for general class ABCDE, lies between +X% and −Y% of the experimental value.

Accuracy of methods for isothermal and adiabatic compressibilities and velocity of sound—Table V

Class Symbol[a]	Kinds of Liquids	N[b]	Avg. % Error[c]
	ISOTHERMAL COMPRESSIBILITY		
Rao-Li Method			
A	All organics	16	−12.4±64.4
A	Organics, excluding oxygen-containing compounds	8	9.62±20.7
AK	Oxygen-containing organics	8	34.5±50.2
Wada Method			
A	All organics	19	−0.03±20.0
ACK	Nonassociated oxygen-containing organics	15	−2.62±12.5
	ADIABATIC COMPRESSIBILITY		
Rao Method			
A	All organics	146	−2.24±7.0
ACEK	Associated, oxygen-containing organics (acids, alcohols, aldehydes)	37	−4.8±11.4
ACK	Nonassociated oxygen-containing organics (ethers, esters, ketones)	39	−2.89±20.1
A	Other organics	71	−1.33±4.0
Wada Method			
A	All organics	132	−17.6±51.9
	VELOCITY OF SOUND		
Rao Method			
A	All organics	134	0.9±22.7
AC	Polar organics	120	1.4±19.8
ACE	Associated organics	46	0.3±14.2
ACN	Halogenated organics	22	4.2±16.6
ACF	Polar hydrocarbons	14	4.3±24.4
AC	Polar organics, except associated, halogen-containing compounds, and hydrocarbons	38	−2.3±20.3
AD	Nonpolar organics	14	−3.7±51.0
Rykov Method			
A	All organics	67	12.2±35.0
AC	Polar organics	65	12.2±35.0
ACE	Associated organics	17	36.8±32.4
ACN	Halogenated organics	8	3.8±42.7
ACF	Polar hydrocarbons	17	4.1±13.1
AC	Polar organics, except associated, halogen-containing ones, and hydrocarbons	23	3.8±26.0
Surface-Tension Correlation			
A	All organics	112	−8.7±52.5
AC	Polar organics	98	−9.0±54.7
ACE	Associated organics	30	7.4±25.3
ACN	Halogenated organics	16	−28.8±80.0
ACF	Polar hydrocarbons	15	4.4±23.3
AC	Polar organics, except associated, halogen-containing ones, and hydrocarbons	30	−19.4±89.0

[a] Symbol definition given in Table IV of Part 8, *Chem. Eng.*, May 19, 1969, p. 194.
[b] Sample population.
[c] The ± value indicates the 95% reliability limits described in the footnote in the left-hand column of this page.

References

1.* Parthasarthy, S., and Bakhshi, N. N., *Indian J. Phys.*, 27, 73 (1953).
2. Partinton, J. R., "An Advanced Treatise on Physical Chemistry," Vol. II, Longmans, Green & Co., London (1951).
3. Rao, R., *Current Sci. (India)*, **9**, 584 (1940).
4. Rao, R. V. G., and Li, J. C. M., *Z. Physik. Chem. Leipzig*, 213, 166 (1960).
5. Reid, R. C., and Sherwood, T. K., "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
6. Rykov, V. I., *Russ. J. Phys. Chem.*, 37, 601 (1963).
7. Rykov, V. I., *Russ. J. Phys. Chem.*, 39, 494 (1965).
8. Sakiadis, B. C., and Coates, J., "A Literature Survey of Ultrasonic Velocities in Liquids and Solutions," Louisiana State University, Engineering Experimental Station, Bull. 46, Baton Rouge, La. (1954).
9. Sakiadis, B. C., and Coates, J., *AIChE J.*, **1**, 275 (1955).
10.* Schaafs, W., *Chem. Abstracts*, **31**: 6072²; **34**: 1889⁵; 5329²; **36**: 6852⁴.
11.* Suryaprakasam, V., *Proc. Indian Acad. Sci.*, **12A**, 341 (1940).
12. Wada, Y., *J. Phys. Soc. Japan*, **4**, 280 (1949).
13.* Weissler, A., *Chem. Abstracts*, **41**: 7185c; **42**: 7590a; **43**: 3256d, 4531i, 6024h; **44**: 6218f; **45**: 8313b.

* Data source.