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THE VOLUME EXPANSION FACTOR FOR LIQUID-SOLID TRANSITION AT THE TRIPLE POINT

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Abstract—The volume expansion factor associated with the liquid-solid transition at the triple point, $\varepsilon = V_{lt}/V_{st}$, is a fluid characterizing parameter that finds utility in the prediction of the transport properties of substances in their dense gaseous and saturated and compressed liquid states. Values of this factor were independently established from the generalized treatment of self-diffusivity, viscosity and thermal conductivity involving information relating to these transport properties for monatomic, diatomic, and polyatomic substances and hydrocarbons of all types of molecular complexity.

These values, derived from each of these transport properties, were found to be consistent and in agreement with each other and corresponding experimental measurements. This factor has been applied to the development of a relationship capable for its generalized prediction using information relating to Z_c, the critical compressibility factor and T_{Rt} the reduced temperature at the triple point.

Values of ε obtained from limited experimental measurements were compared with values predicted by this method and were found to be in close agreement with corresponding values resulting from experimental measurements. Therefore, this development can be made to apply in a generalized manner to all types of substances.

INTRODUCTION

The critical constants of substances have so far proven to be satifactory normalizing parameters for the generalized treatment of thermodynamic and transport properties consistent with the theorem of corresponding states. In this regard, temperature, pressure and volume are ordinarily normalized with corresponding critical temperatures, critical pressures and critical volumes to produce reduced quantities which are then applied to the correlation of these thermodynamic and transport properties. The involvement of these normalized quantities has proven satisfactory for the correlation and prediction of transport properties associated with the dilute and dense gaseous states of fluids; however, its extension of application into the liquid region has so far proven to be of limited utility. Thus for liquids existing at temperatures above their normal boiling point, these generalized methods of correlation have been found to conform reasonably well to the prediction of these transport properties; however, for temperatures below their corresponding normal boiling points, and particularly for conditions approaching the triple point region, these methods fail to account properly for the generalized behavior of self-diffusivity, viscosity and thermal conductivity. This pattern of behavior is not unexpected since the involvement of the critical point stipulates a frame of reference near its vicinity and properly accommodates the dilute and dense gaseous states, but may not necessarily conform to the behavior of liquids at low temperatures and particularly for temperatures approaching the triple point region. Because of this duality in behavior, it could be well argued that the triple point as well constitutes a frame of reference relating to its immediate region in the same manner that the critical point has been found to apply for state conditions in close proximity to it.

Reasons for this disparity may be accounted for the following reasons: in the near vicinity of the critical point, a highly disorganized order of molecular orientation prevails for both saturated liquids and saturated vapors and extends into the dense fluid state provided the temperature and pressure conditions are not significantly removed from this frame of reference. However, with decreasing temperature, and particularly for conditions existing below the normal boiling point, this prevalent randomness gradually begins to disappear with the onset of a new realignment dictated by the specific crystalline configuration of the substance which must be realized as its freezing state is approached. Consequently, the liquid-solid coexistence equilibrium state at the triple point becomes a frame of reference at this phase transition. Therefore, this frame of reference reflects in significance, in the same manner as does the critical point. This argument stipulates that there must exist a dual frame of reference which dictates in what region the critical point or the triple point becomes dominant. Thus, in general, the critical point can be associated with vapor-liquid phase transition while the triple point becomes of significance in the near liquid-solid phase transition.

TREATMENT OF AVAILABLE EXPERIMENTAL DATA

At the present time no rigorous melting theory exists. Moreover, there is not even a generally accepted philosophy that qualitatively reflects the understanding of the physical nature of melting. The unavailability of adequate experimental measurements of substances along their melting curve has been so far largely responsible for the lack of a development relating to the generalized behavior of this region. However, by this time, limited information has appeared in the literature for a few substances to justify a reappraisal of the melting behavior.

Sharma [1] initiates arguments for the development of a corresponding states approach and points that solid molar volumes at their triple point play an important role in describing the thermodynamic behavior in this liquid-solid phase transition. In this connection, Sharma compares calculated solid molar volumes at the triple point with experimental measurements available for twelve substances. Additional information is currently available from the experimental studies of Cheng et al. [2] obtained from their work relating to the melting behavior of methane and nitrogen. Ree et al. [3] report experimental measurements for the molar volumes at the triple point of solid methane, benzene, carbon tetrachloride and carbon dioxide. Supplementary experimental measurements are reported for cyclohexane by Höpfner et al. [4] and for sulfur hexafluoride by Semenova et al. [5]. All these experimental values are presented in Table 1. This table also includes experimental liquid molar volumes at the triple point, v_{lt}, for a number of substances obtained from the comprehensive study of the saturated liquid state of polar and nonpolar substances [6]. If not available, values of v_{lt} can be calculated from the relationship of Rackett [7] applied at the triple point and modified by Spencer and Adler [8] to the expression,

$$v_{lt} = v_c Z_{RA}^{(1-T_R)^{2/7}} \tag{1}$$

where Z_{RA} is a constant specific to a substance. Spencer and Adler present such constants for 165 pure compounds. If Z_{RA} values are not available, the critical compressibility factor, Z_c, proposed by Rackett, can be substituted for it.

The volume expansion associated in the course of melting at the triple point is shown to bear directly on the behavior of self-diffusivity, viscosity and thermal conductivity of the dense gaseous and liquid states of substances of both simple and complex molecular configurations. This volume expansion factor can be defined as,

$$\varepsilon = \frac{v_{lt}}{v_{st}} \tag{2}$$

and applies specifically to the liquid-solid phase transition at the triple point. In their studies relating to the significant structure theory, Zandler et al. [9] investigate the three structurally similar molecules, CO_2, COS and CS_2 and show that some of the thermodynamic and mechanical properties of these compounds in their liquid state are quite dissimilar. For example, the triple point vapor pressures of CO_2, COS and CS_2 are 5. 112, 0.00065 and 0.000018 atm, respectively, compared with typical values near 0.1 atm for most other small molecules. When the temperatue is raised to the triple point, the solid melts undergoing a very large volume and entropy change. Using the data of Zandler et al., the volume expansion factor at the triple point becomes 1.068 for CS_2 and 1.284 for CO_2. This approach was extended in this study to include the limited experimental liquid and solid molar volumes at the triple point available in the literature for a few substances. Values of ε calculated from these experimental measurements are presented in Table 1 for 13 substances.

For the solid-liquid phase transition, the Clapeyron equation offers a means for establishing the volume expansion factor. For this factor at the triple point, the Clapeyron equation takes the form of the following expression,

$$\varepsilon = \frac{1}{1 - \frac{\lambda_f}{v_{lt} T_t} / \left(\frac{\partial P}{\partial T}\right)_t} \tag{3}$$

where the derivative $(\partial P/\partial T)_t$ represents the slope of the fusion curve at the triple point and λ_f is the heat of fusion. Unfortunately, information of this type at this time is available only for a limited number of substances and therefore, at present, equation (3) does not offer a convenient means for the calculation of ε-values.

VALUES FROM TRANSPORT PROPERTIES OF DENSE GASES AND LIQUIDS

For the generalized behavior of self-diffusivity,

Table 1. Information relating to volume expansion factors and solid molar volumes at the triple point.

	Z_c	T_c, K	T_t, K	T_{Rt}	v_{lt}		v_{st}	ζ	ε, Volume expansion factor				
					exp.	eq. (1)	exp.		exp.	D	μ	k	eq. (12)
Monatomic													
Neon	0.298	44.45	24.54	0.5521	16.21	16.41	13.98^a	1.5615	1.15951	1.15120	1.14704	1.14650	1.15781
Argon	0.293	150.86	83.79	0.5554	28.21	28.45	24.98^a	1.4984	1.13658	1.14852	1.14396	1.14786	1.15082
Krypton	0.292	209.41	115.94	0.5537	34.31	34.74	29.66^a	1.4985	1.15678	1.12959	1.15251	1.15159	1.14890
Xenon	0.290	289.75	161.36	0.5569	42.66	43.50	37.10^a	1.4313	1.14987	1.14459	1.13843	1.13986	1.14701
Diatomic													
n-Hydrogen	0.305	33.3	13.947	0.4188	26.06	24.50				1.22091			1.14167
Nitrogen	0.290	126.2	63.14	0.5003	32.29	32.30	29.31^a	1.3500	1.10167	1.11916	1.12160	1.11496	1.13126
Oxygen	0.288	154.58	54.363	0.3517	24.81	24.59		1.2365			1.08855	1.08346	1.09002
Fluorine	0.288	144.30	53.48	0.3706	22.29	22.29					1.08531		1.09434
Hydrocarbon													
Methane	0.289	190.555	90.66	0.4758	35.37	35.67	30.94^d, 31.06^b	1.4069	1.14097	1.13981	1.13654	1.13626	1.12300
Ethylene	0.276	282.40	104.00	0.3683	42.62	42.32	39.06	1.1283	1.08346	1.08532	1.08240	1.08242	1.07178
Ethane	0.274	305.4	89.88	0.2943	45.58	44.96		1.0678		1.06000	1.05413	1.06102	1.04838
Propane	0.271	369.8	85.44	0.2310	60.28	59.41		0.9940		1.01189	1.02204	1.03201	1.02894
n-Butane	0.274	425.18	134.86	0.3172	78.44	79.67		1.0140			1.04468	1.03291	1.05418
n-Pentane	0.269	469.6	143.40	0.3054	95.10	92.98		0.9695		1.05816	1.04017	1.02436	1.04216
n-Hexane	0.263	507.4	177.84	0.3505	113.45	113.84		0.9567		1.05315	1.05231	1.03823	1.04762
Cyclohexane	0.277	553.2	279.83	0.5058	106.30	107.81	101.1^a	1.1380	1.05143	1.07678	1.07635	1.08302	1.11603
Benzene	0.271	562.09	278.693	0.4958	87.31	88.06	77.0^d, 82.82^b	1.1502	1.09260	1.09795	1.10083	1.11264	1.10723
n-Heptane	0.260	540.3	182.57	0.3379	129.20	130.79		0.9480		1.03642	1.04132	1.04423	1.03962
Toluene	0.263	591.79	178.169	0.3011	94.55	94.52		0.9718				1.04825	1.03124
n-Octane	0.255	568.8	216.38	0.3804	150.38	150.34		0.9183		1.05383	1.05560	1.04314	1.05162
n-Nonane	0.250	593.8	219.66	0.3699	165.58	165.23		0.9141		1.04157	1.04557	1.06327	1.04443
n-Decane	0.245	617.6	243.51	0.3943	184.25	183.39		0.8696		1.04683	1.05095	1.04676	1.05490
n-Undecane	0.240	638.8	247.6	0.3876	203.28	197.75		0.8813				1.08998	1.05243
n-Octadecane	0.240	745.0	301.35	0.4045	327.73	330.78					1.04046		1.06146
Miscellaneous													
Ammonia	0.242	405.5	195.41	0.4819	23.11	22.73				1.11728			1.10170
Carbon dioxide	0.274	304.19	216.55	0.7119	37.37	38.85	29.09^b	1.4202	1.28463	1.20829	1.20627	1.20701	1.18665
Carbon disulfide	0.293	552.0	161.3	0.2922	53.06	54.51	49.0^a		1.08285	1.07565			1.09021
Carbon tetrafluoride	0.277	227.6	86.35	0.3794	46.70	46.12				1.07047			1.07660
Chloroform	0.293	536.4	209.6	0.3908	72.57	77.95				1.07732			1.10926
Carbon tetrachloride	0.272	556.40	250.00	0.4493	91.96	92.14	87.1^b	1.0685	1.05580	1.06707	1.07389	1.06883	1.09195
Sulfur hexafluoride	0.267	318.7	222.5	0.6981	–	80.40	68.0^c		1.18235	1.18283			1.18341
Tetramethylsilane	0.273	448.61	182.00	0.4057	114.14	118.26			1.04247	1.06379			1.07873
Fluorobenzene	0.265	560.09	243.0	0.4178	88.12	86.56			1.07629				1.07393
Chlorobenzene	0.265	632.4	227.6	0.3599	95.67	95.73			1.05747				1.05332
Bromobenzene	0.263	670.0	242.3	0.3616	100.79	100.32			1.06416				1.05153
Iodobenzene	0.265	721.0	241.8	0.3354	107.71	107.52			1.05653				1.04511

a) Höpfner et al. (1979), b) Ree et al. (1964), c) Semenova et al. (1977), d) Sharma (1980) viscosity and thermal conductivity of dense gases and liquids, limited by their freezing curves, Lee [10] utilizes the triple point as a frame of reference to normalize these transport properties and generates expressions consistent with the theorem of corresponding states. For self-diffusivity, the expression for all types of substances was found to be,

$$\frac{\tau}{D\delta_t} \times 10^{-5} = \exp(4.0443g^{6.1879}+0.9783g^{0.8604}) - 1 \tag{4}$$

where the normalizing self-diffusivity parameter, $\delta_t = M^{1/2}/T_t^{1/2}v_{lt}^{1/3}$. The global variable, $g=x/\varepsilon^{2.2503/x^{0.7003}}$, requires for its definition information relating to the density and temperature of the fluid and the fluid characterizing parameter, $\varepsilon = v_{lt}/v_{st}$. The variable, $x = \omega/\tau^{0.09w^{3.1}}$, requires that the density and temperature of the fluid be normalized with the corresponding triple point values ($\tau = T/T_t$ and $\omega = \rho/\rho_{lt}$). Thus, with equation (4), a single volume expansion factor can be calculated for a substance from corresponding experimental measurements of self-diffusivity, density and temperature and the normalizing values ρ_{lt} and T_t corresponding to the triple point. Using a nonlinear regression analysis, ε-values were obtained for a number of substances. These values derived from self-diffusivity considerations are reported in Table 1.

An independent approach, utilizing the generalized behavior of viscosity, was also made to establish ε-values. For residual viscosity, the generalized expression has been found to be,

$$(\mu - \mu^*)\gamma_t \times 10^5 = \exp(2.9328g^{8.3264}+4.5424g^{0.9228}) - 1 \tag{5}$$

where the normalizing viscosity parameter, $\gamma_t = v_{lt}^{2/3}/M^{1/2}T_t^{1/2}$. Likewise, the global variable becomes, $g = x/(0.976\varepsilon)^{2.3566/x^{0.6673}}$, where $x = \omega/\tau^{0.07\omega^{2.73}}$. Again, using experimental viscosity measurements and corresponding densities and temperatures, ε-values were obtained for a number of substances. These calculated values are also presented in Table 1.

Following an analogous treatment for residual thermal conductivity, the generalized expression becomes,

$$(k - k^*)\psi_t \times 10^5 = \exp(3.5761g^{0.1602}+2.6963g^{0.9941}) - 1 \tag{6}$$

where the normalizing thermal conductivity parameter, $\psi_t = M^{1/2}v_{lt}^{2/3}/T_t^{1/2}$. However, in addition to ε the establishment of the global variable g for thermal conductivity requires Z_C, the critical compressibility factor. The global variable for this transport property has been found to be, $g = x/\zeta^{x^{-0.13693}}$ where $x = \omega\tau^{0.08327\omega^{1.8158}}$ and ζ is a fluid characterizing parameter specific to a substance. Table 2 presents the deviations between calculated values resulting from equations (4), (5) and (6) and experimental values. Experimental residual thermal conductivities, and corresponding densities and temperatures enabled the calculation of parameter ζ. Values of this parameter resulting from this treatment are presented Table 1. This fluid characterizing parameter has been assumed to depend on Z_c and ε as follows:

$$\zeta = \alpha Z_c^m + \beta\varepsilon^n + \gamma Z_c^p \varepsilon^q \tag{7}$$

where values of Z_c were obtained from the literature and the volume expansion factors, as a first order of approximation, were assumed to be those resulting from self-diffusivity and viscosity measurements. A nonlinear regression analysis for the dependence of ζ on Z_c and ε produced the following values for equation (7):

$$\zeta = \frac{0.4786}{Z_c^{0.1861}} - 0.1131\varepsilon^{7.6003} + 33.7017\,Z_c^{3.3155}\varepsilon^{5.4459} \tag{8}$$

Equation (8) now can be used to calculate values of ε corresponding to thermal conductivities. Using corresponding values of ζ and Z_c, this equation has been applied to calculate values of ε for each substance. These values are also presented in Table 1 and are found to be in reasonably good agreement with the corresponding values of ε resulting directly from the involvement of self-diffusivity and viscosity.

GENERALIZED PREDICTION FOR ε-VALUES FROM THERMODYNAMIC PROPERTIES

The ε-values resulting from the involvement of self-diffusivity, viscosity and thermal conductivity have been related to their corresponding parameters, Z_c, the critical compressibility factor and T_{Rt}, the reduced temperature at the triple point. Using a nonlinear regression analysis produced the following relationship:

$$\varepsilon = \frac{0.08051}{T_{Rt}^{0.3039}} + 4.6237Z_c^{1.4311} + 0.0113\frac{T_{Rt}^{0.8405}}{Z_c^{2.9078}} \tag{9}$$

Values of ε calculated with equation (9) are presented in Table 1 and are compared with corresponding values derived from each of the transport properties. Calculated and actual ε-values are found to be in reasonably good agreement within themselves, thus lending credence to the capability of equation (9) to predict values for this parameter from corresponding Z_c and T_{Rt} values. Therefore, equation (9) summarizes the predictive capability for the estimation of volume expansion factors for the liquid-solid transition at the triple point.

Table 2. Average percent deviations for self-diffusivity, viscosity and thermal conductivity resulting from eqs. (4), (5) and (6).

Substance	Self-diffusivity, eq. (4)		Viscosity, eq. (5)		Thermal conductivity eq. (6)	
	No. Points	% Dev.	No. Points	% Dev.	No. Points	% Dev.
Monatomic						
Neon	30	8.72	81	4.32	6	1.58
Argon	14	10.02	134	3.36	169	4.47
Krypton	19	16.34	19	0.85	147	4.46
Xenon	17	4.43	56	3.34	77	4.39
Diatomic						
n-Hydrogen	25	4.68				
Nitrogen	9	4.46	111	4.74	17	2.13
Oxygen			99	1.61	116	1.57
Fluorine			71	2.23		
Hydrocarbons						
Methane	88	4.83	92	6.27	151	8.30
Ethylene	60	3.44	14	1.26	7	0.69
Ethane	13	9.36	125	1.29	65	6.06
Propane	4	11.65	68	6.38	70	1.42
n-Butane			7	0.65	6	0.91
n-Pentane	7	6.47	243	1.42	16	1.29
n-Hexane	10	7.15	32	1.76	13	0.64
Cyclohexane	39	4.96	25	3.10	49	3.97
Benzene	35	4.85	35	3.35	12	1.75
n-Heptane	9	7.92	36	5.71	50	3.45
Toluene					16	0.86
n-Octane	8	8.78	27	4.47	11	0.31
n-Nonane	8	8.56	17	2.58	64	3.66
n-Decane	9	15.38	136	3.29	9	0.46
n-Undecane					51	3.19
n-Octadecane			8	2.99		
Miscellaneous						
Ammonia	32	8.07				
Carbon dioxide	7	8.41	57	1.39	79	1.22
Carbon disulfide	29	3.15				
Carbon tetrafluoride	4	1.94				
Chloroform	8	1.41				
Carbon tetrachloride	27	2.84	27	1.99	9	2.28
Sulfur hexafluoride	16	8.60				
Tetramethylsilane	42	4.05	43	8.74		
Fluorobenzene	17	7.48				
Chlorobenzene	15	9.17				
Bromobenzene	15	9.04				
Iodobenzene	16	12.63				

CONCLUSION

A comparison of ε-values obtained from self-diffusivity, viscosity and thermal conductivity measurements with those resulting from equation (9) shows a close agreement amongst all three, with the exception of n-hydrogen. For this substance the disagreement between values of 1.22091 and 1.14170, may be due to the higher quantum behavior associated with hydrogen.

It should be noted that the values of the volume expansion factor at the triple point obtained from self-diffusivity, viscosity and thermal conductivity measurements are in close agreement with each other and that this factor presents a unified approach to all three transport properties comparable to the free-volume concept originally advanced by Batschinski [11] and later applied by a number of investigators including Hildebrand [12]. The ability to calculate ε provides an independent approach capable of establishing this triple point parameter with no recourse to experimental measurements.

NOMENCLATURE

g : global variable
k : thermal conductivity, cal/sec cm K
k^* : thermal conductivity of dilute gas, cal/sec cm K
M : molecular weight
m,n,p,q : exponents, equation (7)
P_c : critical pressure, atm
R : gas constant
T : temperature, K
T_c : critical temperature, K
T_t : triple point temperature, K
T_{Rt} : reduced temperature at triple point T_t/T_c
v_c : critical volume, cm^3/g-mole
v_{lt} : liquid molar volume at triple point, cm^3/g-mole
v_{st} : solid molar volume at triple point, cm^3/g-mole
x : density-temperature variable
Z_c : critical compressibility factor, $P_c v_c / RT_c$
Z_{RA} : constant for modified Rackett equation

Greek Letters

α, β, γ : coefficients, equation (7)
γ_t : viscosity parameter, $v_{lt}^{2/3}/M^{1/2}T_t^{1/2}$
δ_t : self-diffusivity parameter, $M^{1/2}/T_t^{1/2}v_{lt}^{1/3}$
D : self-diffusivity, cm^2/sec
ε : volume expansion factor,
ζ : fluid characterizing parameter
λ_f : heat of fusion
μ : viscosity, poises
μ^* : viscosity of dilute gas, poises
ρ : density, g/cm^3
ρ_{lt} : liquid density at triple point, g/cm^3
τ : normalized temperature T/T_t
ψ_t : thermal conductivity parameter, $M^{1/2}v_{lt}^{2/3}/T_t^{1/2}$
ω : normalized density ρ/ρ_{lt}

REFERENCES

1. Sharma, B.K.: Phys. Stat. Sol., **b99,** k121 (1980).
2. Cheng, V.M., Daniels, W.B. and Crawford, R.K.: Phys. Rev., **B11,** 3972 (1975).
3. Ree, T.S., Ree, T. and Eyring, H.: *J. Phys. Chem.*, **68,** 3262 (1964).
4. Höpfner, A., Hörner, C., Abdel-Hamid, A., Schaller, M. and Funk, U.: Ber. Bunsenges. Phys. Chem., **83,** 1031 (1979).
5. Semenova, A.I., Emel'yanova, E.A. and Tsimmerman, S.S.: *Russ. J. Phys. Chem.*, **51,** 1584 (1977).
6. Campbell, S.: Ph. D. Dissertation, Northwestern University, Evanston, U.S.A. (1983).
7. Rackett, H.G.: *J. Chem. Eng.* Data, **15,** 514 (1970).
8. Spencer, C.F. and Adler, S.B.: *J. Chem. Eng.* Data, **23,** 82 (1978)
9. Zandler, M.E., Watson, J.A. Jr. and Eyring, H.: *J. Chem. Phys.*, **72,** 2730 (1968).
10. Lee, H.: Ind. Eng. Chem. Fundam. Submitted for publication (1985).
11. Batschinski, A.J.: *Z. Physik. Chem.*, **84,** 643 (1913).
12. Hildebrand, J.H.: *Science,* **174,** 490 (1971).