

Thermodynamic Properties of Supercooled Steam

F. Bakhtar* and M. Piran†

The paper is concerned with the treatment of flowing high-pressure steam removed from thermodynamic equilibrium. To deal with the thermodynamic properties of supercooled vapour, corrections allowing for the change in the concentration of molecular clusters in the metastable states have been sought. For this purpose the virial equation of state proposed by Vukalovich has been examined and the corrections found to be negligible. Finally, the equations describing the flow of high-pressure steam have been re-examined including the higher virial terms and it is shown that their solution presents no difficulty.

NOTATION

A	area of duct section
a, b	Van der Waal's constants
B_i	$(i + 1)$ th virial coefficient in density series
C	rate of condensational growth of a cluster
c_p, c_v	specific heats of water vapour, kJ/(kg K)
D_i	auxiliary functions defined in the text
d_e	equivalent diameter of duct section
E	rate of evaporational decay of a cluster
f	friction coefficient
F_i	number of clusters containing i molecules per kilogramme in supercooled region
G	Gibb's free energy
g	number of molecules forming a cluster
h	specific enthalpy, kJ/kg
J	rate of formation of critical nuclei, per kilogramme per second
k	the isentropic exponent
k	Boltzmann's constant
l	enthalpy of evaporation
m	mass of one molecule of water
M	mass flow rate
(Ma)	Mach number
N	number of water molecules per kilogramme
N_i	number of clusters containing i molecules per kilogramme in superheated region
p	pressure
q	condensation coefficient
R	gas constant
s	specific entropy, kJ/(kJ K)
T	absolute temperature, K
t	time, s
u	speed of steam, m/s
v	specific volume, m ³ /kg
X, Y	functions defined by eqs. (9) and (10) respectively
ρ	density, kg/m ³
σ	surface tension

L	referring to the liquid phase
n	referring to cluster of n molecules
s	saturation condition

Superscripts

* critical droplet condition

INTRODUCTION

This study originated from the need for a method of treating the flow of high-pressure steam under non-equilibrium conditions. Such problems are experienced in the high-pressure stages of turbines operating in conjunction with water-cooled nuclear reactors, where the steam supply is at high pressure but has very little superheat.

A starting point for the investigation of wetness problems in these turbines is the study of the nucleation process in high-pressure steam and the agreement between the first sets of theoretical and experimental results has been poor (1). In view of the sensitivity of the theoretical solutions to the properties of supercooled steam and the rapid variations in the properties of steam, e.g., its specific heat, near the saturation line, there would be reason to question the justification for extrapolating them into the metastable region. The same doubts would apply equally to any theoretical treatments of the expansion of such wet mixtures when the system is expected to depart from thermodynamic equilibrium.

Properties of steam can be calculated by assuming an equation of state, the saturation line, and the specific heat at zero pressure. Of these, the last two are subject to no uncertainty, thus the problem becomes one of refining a suitable equation of state for application to supercooled vapour. The equations of state used in the calculation of the steam tables available in the literature are normally obtained by starting with an expression based on a physical model and using experimental measurements for calculating its constants. The dominating physical requirement in the present context is that steam, even in the superheated state, contains clusters of water molecules. It is the change in the concentration of these clusters near and below the saturation line which gives rise to the rapid changes in the properties of steam. Thus in the present investigation the distribution of water clusters in steam will be considered first. This will be followed by adopting the resulting relationships

Subscripts

i	referring to cluster of i molecules
G	referring to the vapour phase
g	referring to a cluster containing g molecules

* Department of Mechanical Engineering, University of Birmingham, PO Box 363, Birmingham B15 2TT.

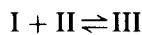
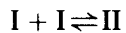
† Department of Mechanical Engineering, Aryamehr University of Technology, Tehran, formerly of the University of Birmingham.

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in the equations describing the flow of high-pressure steam under non-equilibrium conditions.

THE VIRIAL EQUATION OF STATE BY VUKALOVICH

Although most of the equations of state may be written in virial form, that by Vukalovich (2) is particularly relevant to this study because it is based on the Association Theory of Gases. According to this theory a real gas, e.g., steam, is assumed to be a mixture of gases each behaving as a Van der Waal's gas. The individual elementary gases i of the mixture are the clusters of i molecules of the original gas with an equilibrium concentration N_i and behave as independent compound particles. In equilibrium state the decrease of particles of one gas is compensated by association of particles of other gases. The process is analogous to reversible chemical reactions and can be described symbolically as:



etc.

By applying the law of mass action to all these reactions, the concentration of each gas can be found. With the mixture thus defined, the partial pressure p_i of each of the elementary gases will be

$$p_i = \frac{N_i k T}{v - N_i b_i} - \frac{N_i^2 a_i}{v^2} \quad (1)$$

where k is Boltzmann's constant, T the absolute temperature and v the volume occupied by the gas. a_i and b_i are the Van der Waal's constants for one particle of gas i and it is reasoned that they are related to the constants a_1 and b_1 for a single molecule by

$$b_i = i b_1$$

and

$$a_i = i^2 a_1$$

This is substituted into eq. (1) but as Dalton's law does not strictly apply to such a mixture, Vukalovich compensates for it intuitively by writing the summation as:

$$\left(p + \frac{N^2 a_1}{v^2} \right) (v - b_1 N) = \sum_i N_i k T$$

or

$$\left(p + \frac{a}{v^2} \right) (v - b) = \frac{RT}{N} (N_1 + N_2 + \dots + N_n) \quad (2)$$

where $a = a_1 N^2$, $b = b_1 N$ and $N = \sum_n i N_i$ and R is the gas constant.

To obtain the distribution functions N_i , the Helmholtz free energy of the mixture is minimized and after substitution into eq. (2), it is developed to take the virial form:

$$pv = RT \left[1 + \frac{B_1(T)}{v} + \frac{B_2(T)}{v^2} + \dots \right] \quad (3)$$

The virial coefficients are obtained by comparing terms and finally Vukalovich finds the individual terms empirically by comparison with experimental results. In practice it is found that clusters having more than four molecules are comparatively very small in number and

make very little difference to the calculated properties. Therefore only clusters of up to this size are considered. For the purposes of calculation the tables are divided into two ranges of pressure 0.00981–98.1 bars (0.01–100 kg/cm²) and 98.1–981 bars (100–1000 kg/cm²) and two slightly different sets of virial coefficients used for them. Based on these relations Vukalovich published his two steam tables which are in excellent agreement with the skeleton tables (3). The expressions for the virial coefficients in the range 0.00981–98.1 bars are given in Appendix 1.

AN EQUATION OF STATE FOR THE SUPERCOOLED VAPOUR

Because of the success of Vukalovich's method and in the absence of any direct measurements, a case may be made for applying a similar approach to the calculation of the properties of steam in the supercooled region; but with the distribution functions describing the concentration of the molecular clusters adjusted to correspond with the state of the vapour. Using a symbol F_i to denote the concentration of clusters containing i molecules the equation of state would be written as

$$(p + a/v^2)(v - b) = \frac{RT}{N} (F_1 + F_2 + \dots + F_n) \quad (4)$$

where $N = \sum_n i F_i$.

The problem of cluster formation and decay in a supercooled vapour has been studied in the literature in connection with nucleation theory (4) and the results may be used for the present purposes directly.

Using C_i and E_i to denote the rates at which a cluster containing i molecules gains and loses molecules, the main difference between the distribution functions N_i and F_i is that under equilibrium state, although the identity of the individual clusters changes continuously, there is no net overall change in the vapour and

$$C_{i-1} N_{i-1} = E_i N_i \quad (5)$$

In contrast with this, in a supercooled vapour once a cluster has exceeded the critical size it will continue to grow and there will be a net rate J at which these clusters are formed. To achieve this there will be a net difference between the rates of growth and decay of clusters, which under steady state nucleation, will be constant along the embryo chain. Thus in symbols:

$$J = C_{i-1} F_{i-1} - E_i F_i \quad (6)$$

The rate C_i at which a cluster captures molecules may be calculated from the kinetic theory. To calculate E_i , it is reasoned that if the cluster were moved to an environment in thermodynamic equilibrium, then the rates of growth and decay of clusters would be balanced and E_i is calculated from eq. (5). Substitution into eq. (6) after rearrangement gives equations of the form:

$$\left. \begin{aligned} \frac{J}{C_1 N_1} &= \frac{F_1}{N_1} - \frac{F_2}{N_2} \\ \frac{J}{C_{n-1} N_{n-1}} &= \frac{F_{n-1}}{N_{n-1}} - \frac{F_n}{N_n} \end{aligned} \right\} \quad (7)$$

It will be noted that the ratio F_i/N_i decreases with increasing i , thus in the case of supercooled vapour, the

influence of clusters containing more than four molecules can also be regarded as negligible and the expression truncated at F_4 .

For a given state of the vapour, e.g., known temperature and density, the above $n - 1$ equations together with

$$N = \sum_n iF_i$$

are sufficient to solve for the distribution functions F providing J and functions N_i are known. The nucleation current can be calculated from the nucleation theory and to obtain the N_i 's it will be remembered that Vukalovich obtained his virial coefficients by first considering the molecular concentrations. Since his virial coefficients are known, as shown in Appendix 2, using a converse procedure they may be used for the calculation of the cluster distributions $N_1 - N_4$. With these functions determined the calculation of the cluster concentrations $F_1 - F_4$ is relatively simple. The resulting expressions are summarized in Appendix 2. It will be noted that these expressions are in general form while many detailed aspects of the nucleation theory, e.g., any possible variations of the specific surface tension of small agglomerates with size, are still subject to some uncertainty.

The effect of the higher virial coefficients on the expressions for the critical radius, the activation barrier, and the nucleation rate are summarized in Appendix 3. Considering the uncertainties associated with the nucleation theory in an examination of the available results it was found that the use of the classical theory in conjunction with the refinements by Kantrowitz (5) and by Courtney (6), a condensation coefficient of unity and the surface tension of bulk water predicts the available experimental results in low pressure steam reasonably well (7). But both the refinements by Kantrowitz and by Courtney reduce the value of the nucleation rate. It will have been noted from eq. (7) that the decrease in the ratio of distributions F_i/N_i with increasing size of clusters is directly proportional to the nucleation current. Thus as in the present application, the inclusion

of the above refinements would have reduced the difference between the two distributions, it was decided to use the classical expression for the nucleation rate without these corrections.

CALCULATED RESULTS

A typical comparison between the cluster concentrations N and F is given in Table 1. The values of N_i have been obtained for cases in which for the given values of temperature, the vapour density has been chosen to give a pressure of 49.03325 bars (50 kg/cm²). The calculation of the values of F_i has then been carried out by adopting these and the vapour density. By comparing the results in any row, it will be seen that although the change in the cluster concentrations (whether N_i 's or F_i 's) with temperature in the range considered is quite marked, the difference between the two distributions even at considerable amounts of supercooling is small. Similar calculations of cluster concentrations have been carried out for the pressure range 0.98-73.55 bars (8) and a summary of the resulting discrepancies in the pressures is given in Table 2. It will be seen that over the range of conditions likely to be encountered in practice the error in extrapolating the Vukalovich equations is infinitesimal. Even with the extreme amounts of supercooling the error is negligibly small. It may therefore, be concluded that in the absence of direct measurements extrapolation of the Vukalovich equations should provide good estimates of the properties of supercooled steam.

Based on these equations detailed tables of the properties of supercooled steam in the pressure range 0.01-100 bars have been compiled in (8). An abbreviated abstract of these is given in Table 3.

In recommending the use of these tables, it is important to emphasize that they should be used in conjunction with the Vukalovich steam tables. All steam tables are based on a set of mutually consistent equations and although the calculation of the path of any expansion using any one set of tables may give similar results, very serious discrepancies could result if the tables were

Table 1
The N_i and F_i values for supercooled steam at $p = 49.03$ bars (50 kg/cm²)

	$t - t_s$ °C						
	20	10	0	-10	-20	-30	-40
N_1	2.51×10^{25}	2.42×10^{25}	2.32×10^{25}	2.19×10^{25}	2.03×10^{25}	1.82×10^{25}	1.52×10^{25}
F_1	2.51×10^{25}	2.42×10^{25}	2.32×10^{25}	2.19×10^{25}	2.03×10^{25}	1.82×10^{25}	1.52×10^{25}
$N_1 - F_1$	0	0	0	0	0	-9.45×10^{19}	-3.42×10^{21}
N_2	4.13×10^{24}	4.57×10^{24}	5.07×10^{24}	5.66×10^{24}	6.38×10^{24}	7.26×10^{24}	8.46×10^{24}
F_2	4.13×10^{24}	4.57×10^{24}	5.07×10^{24}	5.66×10^{24}	6.38×10^{24}	7.26×10^{24}	8.46×10^{24}
$N_2 - F_2$	0	0	0	0	0	3.80×10^{19}	1.04×10^{21}
N_3	1.29×10^{22}	2.55×10^{22}	5.42×10^{22}	7.66×10^{22}	1.28×10^{23}	2.18×10^{23}	4.00×10^{23}
F_3	1.29×10^{22}	2.55×10^{22}	5.42×10^{22}	7.66×10^{22}	1.28×10^{23}	2.18×10^{23}	4.00×10^{23}
$N_3 - F_3$	0	0	0	0	1.80×10^{16}	4.79×10^{18}	2.08×10^{20}
N_4	9.54×10^{19}	1.09×10^{20}	1.27×10^{20}	1.52×10^{20}	1.30×10^{21}	8.36×10^{21}	2.58×10^{22}
F_4	9.54×10^{19}	1.09×10^{20}	1.27×10^{20}	1.52×10^{20}	1.30×10^{21}	8.36×10^{21}	2.56×10^{22}
$N_4 - F_4$	0	0	0	0	2.81×10^{14}	3.69×10^{18}	1.78×10^{20}
$p(N_i) - p(F_i)$	0	0	0	0	0	-1.07×10^{-04}	-4.68×10^{-03}

Table 2
Errors involved in extrapolation of equation (2)
into the supercooled region

Pressure bar (kg/cm ²)	$T - T_s$ °C				
	-20	-30	-40	-50	-60
0.98 (1)	0	0	0	0	0
4.9 (5)	0	0	0	0	0.003%
9.86 (10)	0	0	0	0.0007%	0.007%
24.50 (25)	0	0	0.002%	0.007%	0.04%
49.03 (50)	0	0.0002%	0.01%	—	—
73.55 (75)	0	0.007%	—	—	—

Table 3
Thermodynamic properties of supercooled steam

T	$p = 0.01$ bar			$T_s = 6.98^\circ\text{C}$		
	v	h	s	c_p	c_v	k
-50.0	102 836	2407.5	8.5418	1.8811	1.4155	1.3271
-40.0	107 469	2426.2	8.6242	1.8747	1.4099	1.3282
-30.0	112 099	2445.0	8.7028	1.8702	1.4059	1.3290
-20.0	116 726	2463.6	8.7781	1.8671	1.4033	1.3294
-10.0	121 356	2482.3	8.8504	1.8653	1.4018	1.3297
0.0	125 975	2501.0	8.9199	1.8644	1.4013	1.3297
+6.0	128 748	2512.1	8.9604	1.8644	1.4014	1.3296

T °C	$p = 0.05$ bar			$T_s = 32.88^\circ\text{C}$		
	v	h	s	c_p	c_v	k
-20	23 273.5	2462.1	8.0307	1.8888	1.4151	1.3294
-10	24 207.3	2480.9	8.1037	1.8834	1.4117	1.3296
0	25 139.4	2499.7	8.1739	1.8797	1.4096	1.3297
+10	26 070.2	2518.5	8.2414	1.8775	1.4087	1.3295
20	26 999.7	2537.3	8.3066	1.8764	1.4087	1.3292
30	27 928.4	2556.1	8.3695	1.8763	1.4095	1.3288
34	28 299.6	2563.6	8.3941	1.8765	1.4100	1.3286

T	$p = 0.1$ bar			$T_s = 45.81^\circ\text{C}$		
	v	h	s	c_p	c_v	k
-10.0	12 064.1	2479.2	7.7788	1.9070	1.4246	1.3296
0.0	12 534.8	2498.2	7.8497	1.8995	1.4204	1.3296
10.0	13 004.1	2517.2	7.9179	1.8941	1.4178	1.3295
20.0	13 472.3	2536.1	7.9836	1.8906	1.4164	1.3292
30.0	13 939.6	2555.0	8.0470	1.8884	1.4161	1.3288
40.0	14 406.0	2573.9	8.1082	1.9975	1.4166	1.3282
46.0	14 685.5	2585.2	8.1440	1.8874	1.4173	1.3279

T °C	$p = 0.5$ bar			$T_s = 81.33$		
	v	h	s	c_p	c_v	k
30	2747.85	2546.1	7.2818	1.9956	1.4737	1.3281
40	2845.31	2566.0	7.3462	1.9783	1.4655	1.3277
50	2942.07	2585.7	7.4082	1.9652	1.4597	1.3272
60	3038.25	2605.3	7.4679	1.9553	1.4558	1.3265
70	3133.93	2624.8	7.5256	1.9479	1.4534	1.3257
80	3229.19	2644.3	7.5814	1.9427	1.4523	1.3249
84	3267.20	2652.0	7.6033	1.9410	1.4522	1.3245

Table 3 Continued

T	p = 1.0 bar			T _s = 99.63		
	v	h	s	c _p	c _v	k
40	1399.56	2555.5	7.0005	2.1120	1.5357	1.3263
50	1450.34	2576.4	7.0662	2.0767	1.5185	1.3261
60	1500.49	2597.0	7.1289	2.0494	1.5056	1.3257
70	1550.13	2617.4	7.1891	2.0281	1.4960	1.3251
80	1599.32	2637.6	7.2471	2.0116	1.4890	1.3244
90	1648.14	2657.6	7.3030	1.9988	1.4840	1.3236
100	1696.4	2677.6	7.3568	1.9890	1.4808	1.3227

T °C	p = 5 bars			T _s = 151.86° C		
	v	h	s	c _p	c _v	k
100	315.99	2627.3	6.5085	2.5839	1.7731	1.3203
110	328.06	2625.6	6.5753	2.4771	1.7256	1.3195
120	339.70	2676.9	6.6381	2.3949	1.6887	1.3186
130	351.00	2700.5	6.6974	2.3305	1.6598	1.3177
140	362.03	2723.6	6.7538	2.2793	1.6370	1.3167
150	373.13	2746.2	6.8082	2.2378	1.6189	1.3147
152	375.25	2750.6	6.8187	2.2306	1.6158	1.3146

T	p = 10.0 bars			T _s = 179.91° C		
	v	h	s	c _p	c _v	k
120	155.13	2612.5	6.1857	3.3569	2.0916	1.3150
130	162.63	2644.6	6.2664	3.0776	1.9866	1.3143
140	169.60	2674.4	6.3392	2.8777	1.9071	1.3136
150	176.20	2702.4	6.4062	2.7287	1.8457	1.3128
160	182.50	2729.1	6.4685	2.6143	1.7976	1.3120
170	188.57	2754.7	6.5271	2.5147	1.7593	1.3112
180	194.4	2779.6	6.5829	2.4533	1.7288	1.3104

T °C	p = 50 bars			T _s = 263.99° C		
	v	h	s	c _p	c _v	k
230	31.83	2624.8	5.6394	7.2347	2.9560	1.2834
240	34.63	2687.4	5.7624	5.5033	2.6718	1.2847
250	36.90	2737.8	5.8596	4.6410	2.4813	1.2855
260	38.88	2781.4	5.9421	4.1112	2.3424	1.2861
264	39.62	2797.5	5.9722	3.9513	2.2968	1.2863

T	p = 100 bars			T _s = 311.06° C		
	v	h	s	c _p	c _v	k
300	16.02	2630.5	5.4454	11.0261	3.3023	1.2699
305	17.06	2678.6	5.5285	8.4516	3.0827	1.2686
310	17.91	2717.3	5.5949	7.1169	2.9227	1.2685
312	18.22	2731.3	5.6187	6.7369	2.8689	1.2685

mixed. To illustrate the point a number of properties of steam have been calculated for a constant pressure of 9.80665 bars (10 kg/cm²) from different tables and the results are compared in Figs. 1-5. The particular equations chosen are: using the second virial coefficient alone, the equations used by Keenan and Keyes (9), Keenan, Keyes, Hill, and Moore (10), and the equations used by Vukalovich. It will be seen that for c_p and k the differences are considerable. Even in the case of specific

entropy, although the differences between the different equations appear relatively small, they are sufficient to cause serious discrepancy if tables are mixed. Another minor complication is that although the sixth edition of the Vukalovich tables is available in English, it has been compiled in the MKS system of units. In view of the widespread use of computers and relative simplicity of the Vukalovich equations, if significant use of the tables is involved it might be easier to carry out the calcula-

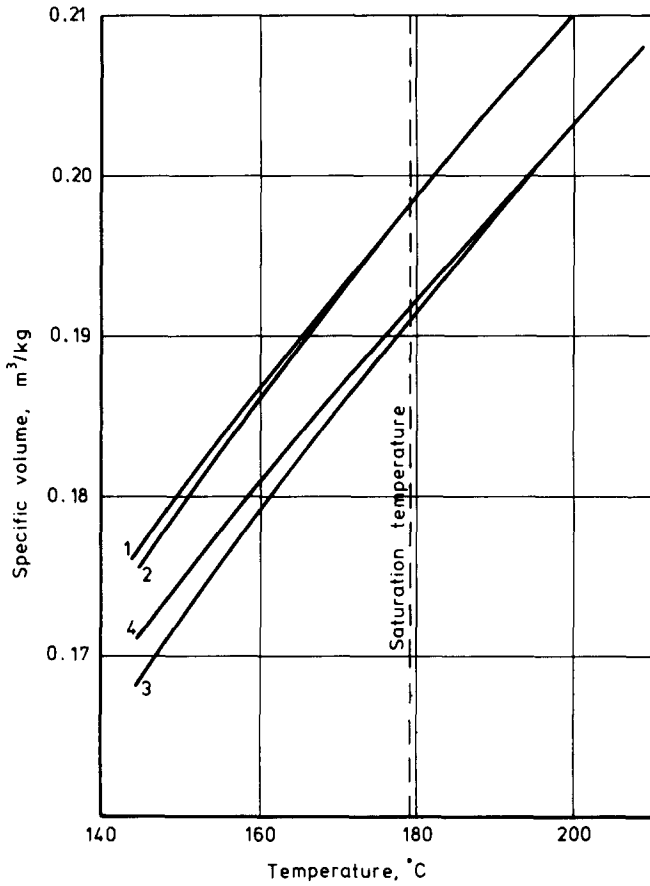


Fig. 1. Comparison between the values of specific volume at 9.8 bars as calculated from different equations. 1—Vukalovich; 2—Keenan, Keyes, Hill, and Moore; 3—Keenan and Keyes; 4—Second virial coefficient alone

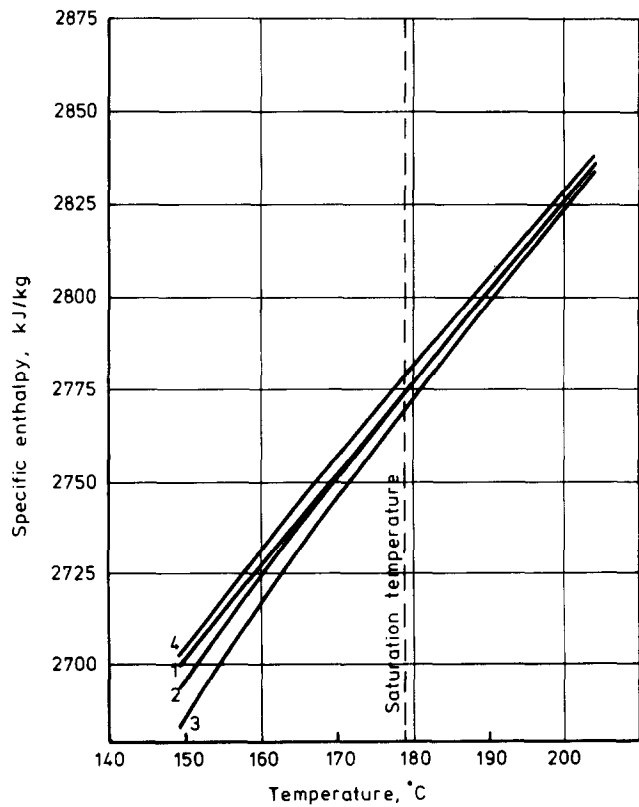


Fig. 2. Comparison between the values of specific enthalpy at 9.8 bars as calculated from different equations. 1—Vukalovich; 2—Keenan, Keyes, Hill, and Moore; 3—Keenan and Keyes; 4—Second virial coefficient alone

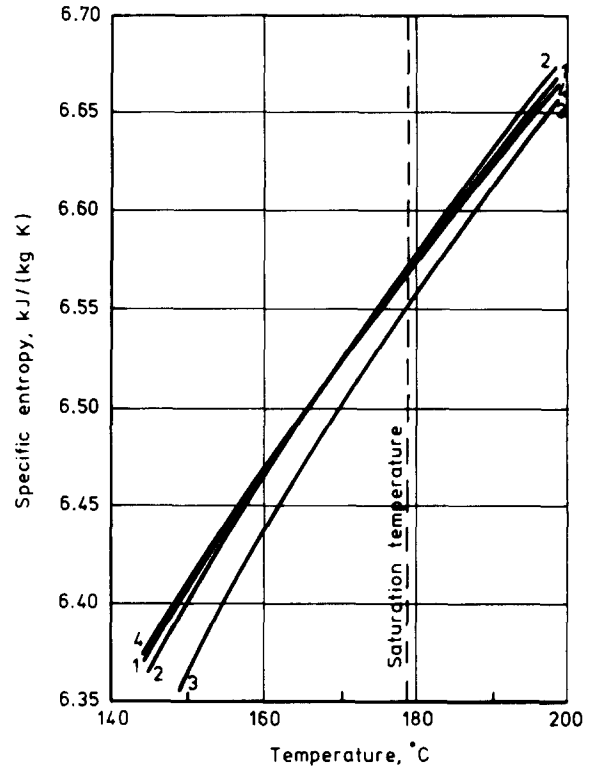


Fig. 3. Comparison between the values of specific entropy at 9.8 bars as calculated from different equations. 1—Vukalovich; 2—Keenan, Keyes, Hill, and Moore; 3—Keenan and Keyes; 4—Second virial coefficient alone

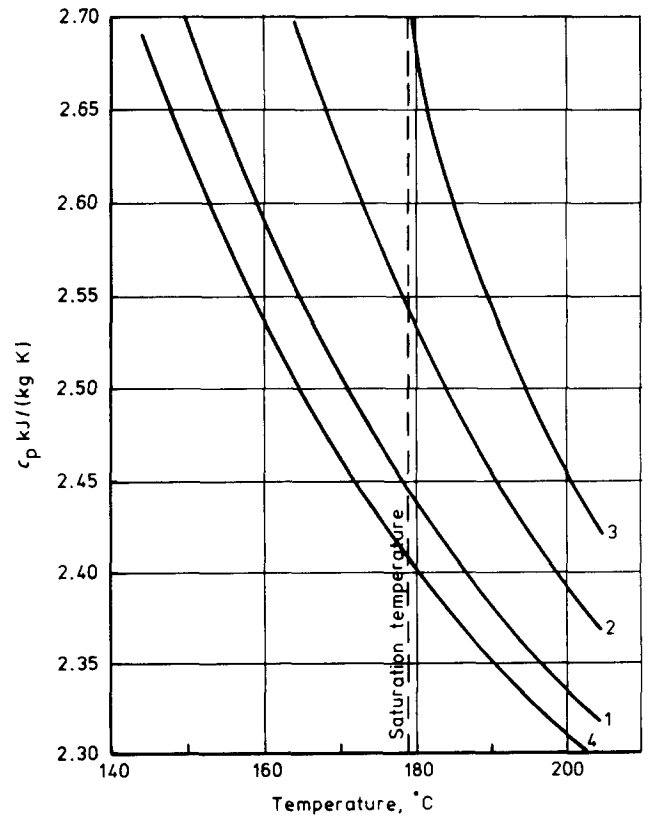


Fig. 4. Comparison between the values of specific heat at constant pressure at 9.8 bars as calculated from different equations. 1—Vukalovich; 2—Keenan, Keyes, Hill, and Moore; 3—Keenan and Keyes; 4—Second virial coefficient alone

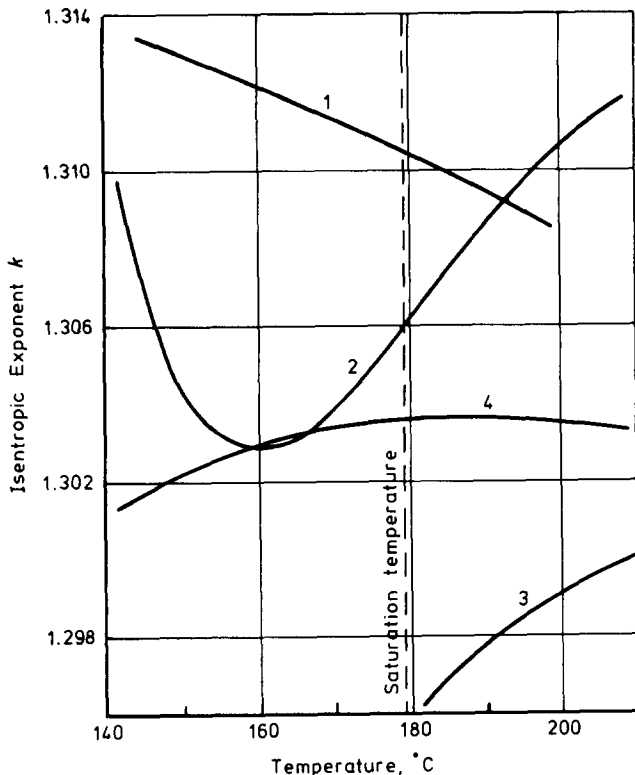


Fig. 5. Comparison between the values of the isentropic exponent at 9.8 bars as calculated from different equations. 1—Vukalovich; 2—Keenan, Keyes, Hill, and Moore; 3—Keenan and Keyes; 4—Second virial coefficient alone

tions by using computer programs. For this purpose the Vukalovich equations for the different properties of steam are also summarized in Appendix 1.

APPLICATION TO FLOWING STEAM

The introduction of the above relationships into the equations describing the flow of steam may now be examined. A similar examination was carried out originally by J. B. Young (11) in which the equation of state was truncated at the second virial coefficient. It will be shown presently that the introduction of the higher virial terms needs no modification of his main flow equations. For ease of description the equations of flow as developed in (1) will be considered and their subsequent refinement discussed.

Equations of Flow

Considering the one-dimensional flow of steam over an incremental distance dx along a duct axis in which the pressure, flow area, velocity, density, temperature, and mass flow rate change from p , A , u , ρ , T , and M to $p + dp$, $A + dA$, $u + du$, $\rho + d\rho$, $T + dT$, and $M + dM$ respectively, the equations of flow may be developed as follows.

Equation of Mass Continuity

Assuming the volume occupied by the liquid phase to be negligible in comparison with that by vapour, the continuity equation may be written as:

$$\frac{d\rho_G}{\rho_G} + \frac{dA}{A} + \frac{du}{u} + \frac{dM_L}{M - M_L} = 0 \quad (8)$$

where suffices G and L refer to the vapour and liquid phases respectively and symbols without suffix refer to the whole flow.

This equation is not affected by the introduction of the higher virial terms.

Equation of State

Defining

$$X = \frac{\rho_G}{p} \left(\frac{\partial p}{\partial \rho_G} \right)_{T_G} \quad (9)$$

and

$$Y = \frac{T_G}{p} \left(\frac{\partial p}{\partial T_G} \right)_{\rho_G} \quad (10)$$

The equation of state may be written as:

$$\frac{dp}{p} - X \frac{d\rho_G}{\rho_G} - Y \frac{dT_G}{T_G} = 0 \quad (11)$$

The actual expressions for X and Y depend on the equation of state and are given in Appendix 1. Thus with the introduction of the new definitions for X and Y the form of the equation of state used in (1) remains unchanged.

Vapour Phase Mach Number

In the treatment it is algebraically convenient to work in terms of the frozen speed of sound. Defining

$$(Ma)^2 = \frac{u^2}{kp/\rho_G} \quad (12)$$

differentiation gives

$$\frac{2 d(Ma)}{(Ma)} = \frac{2 du}{u} + \frac{d\rho_G}{\rho_G} - \frac{dp}{p} \quad (13)$$

Equation of Momentum

Application of Newton's second law to the control volume, assuming a friction factor f , equivalent duct diameter de and no slip between the phases yields:

$$\frac{dp}{p} = -k(Ma)^2 \frac{du}{u} - k(Ma)^2 \frac{f}{2de} dx \quad (14)$$

Thus the form of momentum equation remains unchanged.

Energy Equation

The steady state energy equation for adiabatic flow through the control volume may be written as:

$$u du + dh_G - \frac{d(lM_L)}{M} = 0 \quad (15)$$

where $l = h_G - h_L$ and is the energy given up by vapour on condensing. The term dh_G may be written as:

$$dh_G = c_p dT_G + \left[v_G - T_G \left(\frac{\partial v_G}{\partial T_G} \right)_p \right] dp \quad (16)$$

Using the new definitions of X and Y it may be shown that

$$v_G - T_G \left(\frac{\partial v_G}{\partial T_G} \right)_p = \frac{1}{\rho_G} \left(1 - \frac{Y}{X} \right) \quad (17)$$

which is the form adopted in reference (1). c_p may be substituted from eq. (A1.8), but because of the need to relate the product $c_p T_G$ to the speed of sound a relationship between c_p and k is desirable. For this purpose writing

$$k = \frac{\rho_G}{p} \left(\frac{\partial p}{\partial \rho_G} \right)_T \frac{c_p}{c_v}$$

and

$$c_p - c_v = -\frac{T_G}{\rho^2} \left(\frac{\partial p}{\partial T_G} \right)_{\rho_G} \left(\frac{\partial \rho_G}{\partial T_G} \right)_p$$

substituting from eqs. (9) and (10), simplifying, and rearranging results in

$$c_p = \frac{k}{k-X} \frac{Y^2}{X} \frac{p}{\rho_G T_G} \quad (18)$$

Then substituting eqs. (16) and (17) into eq. (15) and dividing throughout by $c_p T_G$, after substitution from eq. (18) and rearrangement yields:

$$\frac{dT_G}{T_G} + \left(\frac{k-X}{Y^2} \right) (Ma)^2 \frac{du}{u} + \left(\frac{k-X}{k} \right) \left(\frac{X-Y}{Y^2} \right) \frac{dp}{p} - \frac{d(lM_L)}{Mc_p T_G} = 0 \quad (19)$$

which apart from the change in the expressions for X , Y , and c_p is identical in form to the energy equation in reference (1).

It is therefore seen that providing X , Y , and c_p are calculated from eqs. (A1.13), (A1.14), and (A1.8), the form of the original treatment for the solution of the gas dynamic and droplet growth equations remains unchanged. Furthermore, because the additional terms do not involve any new iterative procedures, their effect on increasing the computation times is not very great.

The above modifications to the treatment have been only part of the investigations into the initial differences between theory and experiment in the nucleation studies. Some modifications of the experimental apparatus have also been carried out. It is hoped that the causes of the discrepancy have been resolved and a full set of experimental and theoretical results will be available for publication in the near future.

SUMMARY OF CONCLUSIONS

Near and below the saturation line there is a rapid change in the relative concentration of molecular clusters within steam which leads to the changes in its thermodynamic properties. Indiscriminate extrapolation of equations not allowing for these changes can lead to serious errors.

In the absence of any direct measurements of the properties of steam in metastable states, the use of the virial equation of state developed by Vukalovich is expected to give reasonable results.

The expressions for the thermodynamic properties of steam based on the Vukalovich virial equation of state are relatively simple and can be included directly into the equations describing the flow of high-pressure steam without increasing the mathematical complications.

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APPENDIX 1 THE VUKALOVICH EQUATIONS FOR THE THERMODYNAMIC PROPERTIES OF STEAM IN THE RANGE 0.01-100 kg/cm² AND 0-700°C

1 The Virial Coefficients

$$B_1 = -\frac{e}{RT} - \phi_1 + b \quad (A.1.1)$$

$$B_2 = -b\phi_1 + 4\phi_1^2\phi_2 \quad (A.1.2)$$

$$B_3 = 32b\phi_1^2\phi_2 \quad (A.1.3)$$

$$B_4 = 0 \quad (A.1.4)$$

$$B_5^\dagger = -4n\phi_1^2\phi_2 \quad (A.1.5)$$

where

$$\phi_1 = \frac{CR}{T^{w_1}} \quad (A.1.6)$$

$$\phi_2 = 1 - \frac{K}{T^{w_2}} \quad (A.1.7)$$

and

$$e = 63.2 \text{ m}^5/(\text{kg s}^2)$$

$$b = 0.00085 \text{ m}^3/\text{kg}$$

$$C = 0.3977 \times 10^6$$

$$R = 461.4 \text{ J}/(\text{kg K})$$

$$K = 22.7$$

† Although this sixth virial coefficient has been given by Vukalovich, it makes no difference to the calculated results and can be safely excluded.

$$n = 0.3557 \times 10^{-7}$$

$$m_1 = 1.968$$

$$m_2 = 2.957$$

$$W_1 = \frac{3 + 2m_1}{2}$$

$$W_2 = \frac{3m_2 - 4m_1}{2}$$

2 Thermodynamic Properties

With the virial coefficients defined, the corresponding relations for the thermodynamic properties usually tabulated are as follows:

$$c_p = -RT \left\{ \frac{1}{T} \left[\frac{1}{v} \frac{dB_1}{dT} + \frac{1}{2v^2} \frac{dB_2}{dT} + \frac{1}{3v^3} \frac{dB_3}{dT} \right] + \left[\frac{1}{v} \frac{d^2B_1}{dT^2} + \frac{1}{2v^2} \frac{d^2B_2}{dT^2} + \frac{1}{3v^3} \frac{d^2B_3}{dT^2} \right] \right\} + 1.1111 + 0.00071T + \frac{6992}{T^2} \frac{\text{kJ}}{\text{kg K}} \quad (\text{A.1.8})$$

$$c_v = -2RT \left\{ \frac{1}{T} \left[\frac{1}{v} \frac{dB_1}{dT} + \frac{1}{2v^2} \frac{dB_2}{dT} + \frac{1}{3v^3} \frac{dB_3}{dT} \right] - \frac{1}{2} \left[\frac{1}{v} \frac{d^2B_1}{dT^2} + \frac{1}{2v^2} \frac{d^2B_2}{dT^2} + \frac{1}{3v^3} \frac{d^2B_3}{dT^2} \right] \right\} + 1.1111 + 0.00071T + \frac{6992}{T^2} \frac{\text{kJ}}{\text{kg K}} \quad (\text{A.1.9})$$

$$h = -RT \left[\frac{1}{v} \frac{dB_1}{dT} + \frac{1}{2v^2} \frac{dB_2}{dT} + \frac{1}{3v^3} \frac{dB_3}{dT} \right] + \left[1.1111T + 3.5588 \times 10^{-4}T^2 - \frac{6992}{T} \right] + pv + 2070.54 \text{ kJ/kg} \quad (\text{A.1.10})$$

$$s = 0.3153 + 1.1111 \ln T + 0.00071T - \frac{6992}{T^2} + R \left[\left(\ln v - \frac{B_1}{v} - \frac{B_2}{2v^2} - \frac{B_3}{3v^3} \right) - T \left(\frac{1}{v} \frac{dB_1}{dT} + \frac{1}{2v^2} \frac{dB_2}{dT} - \frac{1}{3v^3} \frac{dB_3}{dT} \right) \right] \quad (\text{A.1.11})$$

$$k = \frac{v}{p} \left[RT \left(\frac{1}{v^2} + \frac{2B_1}{v^3} + \frac{3B_2}{v^4} + \frac{4B_3}{v^5} \right) \right] \cdot \frac{c_p}{c_v} \quad (\text{A.1.12})$$

APPENDIX 2 CALCULATION OF DISTRIBUTION FUNCTIONS OF MOLECULAR CLUSTERS IN TERMS OF THE VIRIAL COEFFICIENTS

1 The Equilibrium Concentrations

Starting with eq. (2) and dividing each N_i by N ($\equiv \sum_n iN_i$) it is possible to expand the equation and by comparing terms to obtain expressions for these functions in terms of the virial coefficients but the solution will involve elaborate series. It was found that by introducing the following set of auxiliary variables the calculations could be carried out directly. Truncating the influence of the clusters at $n = 4$ and defining

$$D_1 = \frac{(N_2/N_1)}{1 + 2(N_2/N_1)} \quad (\text{A.2.1})$$

$$D_2 = \frac{(N_3/N_1)(1 - 2D_1)}{1 + 3(N_3/N_1)(1 - 2D_1)} \quad (\text{A.2.2})$$

$$D_3 = \frac{(N_4/N_1)(1 - 2D_1)(1 - 3D_2)}{1 + 4(N_4/N_1)(1 - 2D_1)(1 - 3D_2)} \quad (\text{A.2.3})$$

Expressions for N 's may be obtained in terms of D 's. Expanding

$$\frac{1}{v-b} = \frac{1}{v} \left(1 + \frac{b}{v} + \frac{b^2}{v^2} + \frac{b^3}{v^3} \right) \quad (\text{A.2.4})$$

substituting the results into eq. (2), expanding, collecting terms, and comparing with eq. (3) will give the virial coefficients in terms of the D 's. But since the virial coefficients are known the three equations may be used to obtain the following relationships:

$$D_1 = - \left(B_1 + \frac{e}{RT} - b \right) / v \quad (\text{A.2.5})$$

$$D_2 = - (B_2 + bD_1v - b^2) / [(2 - 3D_1)v^2] \quad (\text{A.2.6})$$

$$D_3 = - \frac{[B_3 + b^2D_1v + b(2 - 3D_1)D_2v^2 - b^3]}{(3 - 4D_1 - 8D_2 + 12D_1D_2)v^3} \quad (\text{A.2.7})$$

Finally, eqs. (A.2.1), (A.2.2), and (A.2.3) may be solved with $N = \sum_n iN_i$ to give the following expressions for the distribution functions N :

$$N_4 = ND_3 \quad (\text{A.2.8})$$

$$N_3 = (N - 4N_4)D_2 \quad (\text{A.2.9})$$

$$N_2 = (N - 4N_4 - 3N_3)D_1 \quad (\text{A.2.10})$$

$$N_1 = N - 2N_2 - 3N_3 - 4N_4 \quad (\text{A.2.11})$$

For given values of density and temperature, values of pressure calculated by using the above results in eq. (2) as tests of consistency are in complete agreement with those calculated directly from the virial equation as well as Vukalovich's tables.

2 Cluster Concentrations in Supercooled Vapour

For supercooled vapour in a given state, e.g., known density and temperature, the nucleation current is calculated which together with the above values of N_1-N_4

may be substituted in eqs. (7) and together with $N = \sum_i iF_i$ solved to give the values of the cluster concentrations as follows:

$$F_1 = N_1 \left\{ 1 + 2 \frac{N_2}{N} \left(\frac{J}{C_1 N_1} \right) + 3 \frac{N_3}{N} \left(\frac{J}{C_1 N_1} + \frac{J}{C_2 N_2} \right) + 4 \frac{N_4}{N} \left(\frac{J}{C_1 N_1} + \frac{J}{C_2 N_2} + \frac{J}{C_3 N_3} \right) \right\} \quad (\text{A.2.12})$$

$$F_2 = N_2 \left(\frac{F_1}{N_1} - \frac{J}{C_1 N_1} \right) \quad (\text{A.2.13})$$

$$F_3 = N_3 \left[\frac{F_1}{N_1} - J \left(\frac{1}{C_1 N_1} + \frac{1}{C_2 N_2} \right) \right] \quad (\text{A.2.14})$$

$$F_4 = N_4 \left[\frac{F_1}{N_1} - J \left(\frac{1}{C_1 N_1} + \frac{1}{C_2 N_2} + \frac{1}{C_3 N_3} \right) \right] \quad (\text{A.2.15})$$

APPENDIX 3 NUCLEATION EQUATIONS WITH HIGHER VIRIAL COEFFICIENTS

The change in the free energy ΔG_r of a mass of vapour at p and T_G condensing to a droplet of radius r may be written as:

$$\Delta G_r = 4\pi r^2 \sigma + \frac{4}{3}\pi r^3 \rho_L \Delta G_1 \quad (\text{A.3.1})$$

where σ is the surface tension, ρ_L the density of the liquid, and taking account of the second, third, and fourth virial coefficients, ΔG_1 becomes

$$\Delta G_1 = RT_G \left\{ -\ln \frac{\rho}{\rho_s(T_G)} + 2B_1[\rho_s(T_G) - \rho] + \frac{3}{2} B_2[\rho_s^2(T_G) - \rho^2] + \frac{4}{3} B_3[\rho_s^3(T_G) - \rho^3] \right\} \quad (\text{A.3.2})$$

where $\rho_s(T_G)$ is the density of saturated vapour at temperature T_G . For given vapour conditions ΔG_1 is a constant and if the variations of σ with radius can be neglected ΔG_r has a maximum

$$\Delta G^* = \frac{16\pi\sigma^3}{3\rho_L^2(\Delta G_1)^2} \quad (\text{A.3.3})$$

occurring at

$$r^* = \frac{2\sigma}{\rho_L \Delta G_1} \quad (\text{A.3.4})$$

Steady State Nucleation Rate

In the derivation of the classical nucleation rate (4) the reasoning is general up to the expression

$$J = \frac{C_g^* N \exp[-\Delta G^*/kT]}{(2\pi k T_G / Z)^{1/2}} \quad (\text{A.3.5})$$

where

$$Z = - \left(\frac{\partial^2 \Delta G}{\partial^2 g} \right)_{g=g^*}$$

The only terms affected by the virial coefficients in the further development of the analysis are Z and C_g^* . However, by working in terms of density, the form of the expressions describing these terms will be unaltered, the following relations being the result.

$$Z = \frac{2}{9} \left[\frac{36\pi m^2}{\rho_L^2} \right]^{1/3} \frac{\sigma}{g^{*4/3}} \quad (\text{A.3.6})$$

where m is the mass of one molecule of water and

$$C_g = q \frac{4\pi r^2}{m} \rho_G \left(\frac{RT_G}{2\pi} \right)^{1/2}$$

where q is the condensation coefficient and is defined as the fraction of molecular collisions that condense.