UDC 661.723.7.08:547.213

V. K. Gorchakovskii, V. E. Zadov, and V. N. Podvezennyi

The following properties of Freon 216 are determined over a wide temperature range: density of the liquid and its saturated vapor; surface tension on the boundary with the saturated vapor; liquid dynamic viscosity; saturated vapor pressure. In addition, the critical temperature and fusion temperature are determined.

Introduction. Freens which reach the upper layers of the atmosphere dissociate under the action of UV radiation, breaking C-Cl bonds, yielding the radicals Cl, which in turn catalytically destroy ozone. Destruction of the ozone layer definitely degrades our ecology. Bearing this in mind, it becomes important to study those Freens whose molecules have a minimum number of chlorine atoms, but possibly, higher molecular weight. This decreases influx to the stratosphere, since according to the hypsometric law, such molecules decrease exponentially with increase in molecular mass [1].

To a certain degree these requirements are met by Freon 216 $(C_3Cl_2F_6)$, a substance the use of which is not currently limited [2]. Therefore, a study of the properties of Freon 216 which determine its practical usefulness is necessary.

The density of liquid Freon 216 and its saturated vapor pressure were determined pycnometrically. Glass pycnometers having various liquid/gas phase ratios were used. For calibration purposes the pycnometers were filled with mercury and temperature stabilized at 20 and 80°C. The mercury column height was measured by a cathetometer. In this manner the dependence of mercury level height upon volume was determined for each pycnometer. The correlation coefficients obtained for the regression equations proved to be quite large (>0.99999). The liquid phase volumes at temperatures differing from those indicated were found by use of the volume expansion coefficient of glass, which was calculated for the temperatures in question.

Experiments to determine density were carried out in the following manner. The necessary quantity of Freon was poured into the pycnometer, after which the latter was hermetically sealed, cooled to -196 °C, evacuated to a residual pressure of 10^{-3} mm Hg, and sealed. The pycnometer was then brought to thermal equilibrium with the system, after which the cathetometer was used to determine the liquid level. Temperature was maintained to an accuracy of ± 0.05 °C. After completion of the measurements the pycnometer was weighed, then emptied, washed, and weighed again empty, as well as filled with distilled water. In this procedure the lift force of the atmosphere on the objects being weighed, as well as the brass scale weights, was considered.

Calculations to determine uncertainties in density were performed by the usual method [3], with consideration of the fact that the density values of both liquid and gaseous Freon were determined by six values: the Freon mass, and volume of liquid and vapor phases in each of two pycnometers.

The experimental results on density determination are shown in Table 1.

Surface tension of Freon 216 on the liquid-saturated vapor boundary was determined by the capillary lift method. The theory underlying this phenomenon provides the following relationship, valid for temperatures much less than critical given complete wetting [4]

 $\sigma = rh\rho g/2.$

Three glass capillaries were used. Uniformity of diameter was checked by displacing a mercury column while measuring its length with a microscope. In all the capillaries diameter

Siberian Technological Institute, Krasnoyarsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 59, No. 1, pp. 122-126, July, 1990. Original article submitted May 5, 1989.

t P.L P.V	$\begin{array}{ } -20\\ 1693, 3\pm 0, 13\\ -\end{array}$	$1668, 6\pm 0, 13$	$0\\1643,2\pm0,13\\2,5784\pm0,016$	$ \begin{array}{c c} 10 \\ 1616,8\pm0,12 \\ 3,8548\pm0,016 \end{array} $
t ρ _ν ρ ρ _v	$\begin{array}{ c c c c } & 20 \\ & 1590, 2\pm0, 12 \\ & 5,5315\pm0, 016 \end{array}$	$30 \\ 1563, 1\pm0, 11 \\ 7, 7568\pm0, 015$	$\begin{array}{r} 40\\1534,2{\pm}0,12\\10,246{\pm}0,015\end{array}$	$50\\1505,0\pm0,12\\13,927\pm0,015$
t ρ:ջ ρ _v	$\begin{array}{c} 60 \\ 1475, 2\pm 0, 11 \\ 19, 698\pm 0, 12 \end{array}$	$70 \\ 1444, 1\pm0, 11 \\ 25, 794\pm0, 11$	$ 80 1411,9\pm0,10 33,237\pm0,11 $	90 1377,9 \pm 0,11 42,376 \pm 0,11
t ρ ₀ ρ _v	$ 100 1341,3\pm0,10 53,669\pm0,11 $	$110 \\ 1302,3\pm 0,099 \\ 67,554\pm 0,10$	$120 \\ 1262,7\pm0,093 \\ 84,215\pm0,10$	$130 \\ 1221, 6\pm 0, 087 \\ 101, 987\pm 0, 097$

TABLE 1. Density of Freon 216 and Its Saturated Vapor at Various Temperatures

TABLE 2. Surface Tension of Freon 216 at Various Temperatures. References: CCl₄ (column I) and n-Heptane (Column II)

Temp., °C	σ-10°, N/m		Temp.,	$\sigma \cdot 10^3$, N/m	
	I	I 1	°C	I	11
0 10 20 30 40	$16,06\pm0,03\\14,97\pm0,03\\13,97\pm0,03\\12,87\pm0,02\\11,85\pm0,02$	$\begin{array}{c} 16,09{\pm}0,03\\ 15,00{\pm}0,04\\ 13,95{\pm}0,03\\ 12,88{\pm}0,02\\ 11,83{\pm}0,02 \end{array}$	50 60 70 80	$10,87\pm0,029,80\pm0,028,85\pm0,027,88\pm0,01$	$10,89\pm0,029,77\pm0,028,77\pm0,027,75\pm0,01$

nonuniformity did not exceed 0.03%. The capillaries were sealed in an ampul. Reference liquids used were chemically pure grade carbon tetrachloride and reference grade n-heptane. Ampul filling and sealing were carried out in a manner similar to that described for the pycnometers above.

Measurements were performed in the following manner. After maintenance at a certain temperature liquid level height in all capillaries was measured by a cathetometer, and the level difference Δh_{i-1} between each capillary and the first, which had the largest diameter, was determined. The Δh_{i-1} values obtained for the reference liquid were used to calculate the quantity A_{i-1} characterizing the given pair of capillaries:

$$A_{i-1} = \sigma_0 / \rho_0 \left(\Delta h_{i-1} \right)_0,$$

where the subscript 0 denotes the reference liquid.

Then, using the values of A_{i-1} the surface tension of the Freon was calculated:

$$\sigma = \rho \Delta h_{i-1} A_{i-1}.$$

Measurements were performed seven times at each temperature, after which the Δh_{i-1} values were averaged.

Uncertainties in surface tension measurements were calculated by the standard method of [3], commencing from the fact that they depend on the following factors: uncertainties in determining Freon density, cathetometer readings, and uncertainties in determining A_{i-1} . The latter in turn depend on two factors: nonuniformity in capillary diameter and uncertainties in determining the reference liquid lift height differences.

The experimental results are presented in Table 2.

The dynamic viscosity of Freon 216 was determined by the relative method. A Ubellode glass capillary viscosimeter with pendant level was prepared. The capillary diameter was 0.3 mm, with working volume of 20 cm³. The liquid escape time was determined with an F5041 electronic counter, started and stopped manually. The reference liquid chosen was carbon tetrachloride, which has physicochemical properties close to those of Freon 216, thus allowing us to neglect a correction for kinetic energy of the jet [5]. The viscosimeter was

eratures			
Temp., °C	η·10 ⁶ , Pa *sec	Temp., °C	η.106, Pa·sec
$ \begin{array}{r} -20 \\ -10 \\ 0 \\ 10 \\ 20 \\ 30 \\ 40 \\ 50 \\ \end{array} $	$ \begin{array}{r} 1176\\ 980\\ 831\\ 713\\ 621\\ 544\\ 482\\ 423 \end{array} $	60 70 80 90 100 110 120 130	380 339 300 272 242 222 195 178

TABLE 3. Freon 216 Viscosity at Various Temperatures

TABLE 4. Saturated Vapor Pressure of Freon 216

Temp., °C	P, Pa	Temp., °C	P, Pa
10 20 30 40 50	$\begin{array}{r} 42500 \pm 270 \\ 62360 \pm 50 \\ 88960 \pm 570 \\ 124380 \pm 440 \\ 170400 \pm 700 \end{array}$	60 70 80 90	$\begin{array}{c} 228200\pm850\\ 300700\pm170\\ 389900\pm1300\\ 497100\pm170\\ \end{array}$

filled with liquid as described above. The dynamic viscosity was then calculated from the expression

$\eta = \eta_0 \tau \rho / \tau_0 \rho_0.$

A total of 10 measurements were performed at each temperature. The CCl_4 density and viscosity were taken from [6]. The Freon density was substituted in the above expression with consideration of the repulsive force acting on the vapor. Results are presented in Table 3.

It should be noted that the literature lacks reliable data on CCl₄ viscosity in the temperature interval -20-0°C, so at those temperatures the Freon viscosity was calculated using extrapolated values of the viscosimeter constant $\eta_0/\tau_0\rho_0$.

It is known from the literature that the capillary viscosimeter method involves an uncertainty of 1-1.5% although the escape time and liquid density can be determined with significantly greater accuracy (0.1-0.2%).

The saturated vapor pressure of Freon 216 was measured at various temperatures with equipment which was described in [7]. Experimental results are presented in Table 4.

The critical temperature of Freon 216 was determined from the moment of disappearance of the liquid meniscus in the sealed glass ampul as temperature is increased and the moment of meniscus appearance as the temperature is decreased. The quantity of Freon in the ampul was chosen such that upon approach to the critical temperature the meniscus was located at approximately the midpoint of the ampul. The ampul was sealed as described above. Glycerine was used for the temperature stabilizing liquid bath and heated by a nichrome filament. Near the critical point the temperature was changed very slowly, approximately 0.1°C over 10 min. It should be noted that immediately after disappearance of the meniscus there was a critical opalescence in the form of a bluish cloud, with a similar phenomenon occuring before reappearance of the meniscus.

The value $t_{cr} = 178.7 \pm 0.1^{\circ}C$ was obtained.

The Freon 216 fusion temperature was determined by taking cooling curves. The Freon was placed in a Dewar flask, cooled by liquid nitrogen. The specimen temperature was recorded by a platinum resistance thermometer, having a nominal resistance of 50 Ω . The resistance was measured by an R-5058 digital acceleration bridge, numerical values being automatically printed out every 60 sec.

After taking several cooling curves the value $t_f = -127.7 \pm 0.6$ °C was obtained.

<u>Conclusions</u>. The data presented above show that the physical properties of Freon 216 are close to those of the frequently used Freons 113 and 114B2, and may be used in place of the latter.

NOTATION

σ, liquid surface tension; r, capillary radius; h, capillary ascent height; ρ, density, kg/m³; g, acceleration of gravity; η, dynamic viscosity; τ, outflow time; t, temperature, °C.

LITERATURE CITED

1. S. S. Voyutskii, Course in Colloidal Chemistry [in Russian], Moscow (1964).

2. Protocol on Ozone-Destroying Materials, Montreal (1987).

S. G. Ruzhnikov, O. V. Yangolov, M. L. Shchipko,

3. J. Squires, Practical Physics [Russian translation], Moscow (1971).

4. K. F. Zhigach, Zavod. Lab., No. 6, 699-703 (1937).

5. É. Gatchek, Viscosity of Liquids [in Russian], Moscow-Leningrad (1935).

6. Handbook of Chemistry, Volume 1 [in Russian], Moscow-Leningrad (1962).

7. I. I. Perel'shtein, Methods for Experimental Study of the Properties of Cooling Agents [in Russian], Moscow (1963).

OPTIMAL STARTUP CONDITIONS OF FLUIDIZED-BED BOILER

and S. L. Gritsko

UDC 662.62:65.096.5

A mathematical model is developed permitting optimization of the startup of fluidized-bed equipment in which an exothermal reaction is occurring, by numerical-experiment method. The results obtained are tested for a semicommercial 8-MW power boiler.

Startup of power boilers with a fluidized bed (as well as gas generators, calcination furnaces, and steam boilers) from the cold state is sufficiently complex and, as a rule, includes the operation of heating the bed material and the apparatus to a definite temperature using an auxiliary (startup) fuel [1-3].

The aim of the present investigation is to optimize the startup conditions (on account of reduction in length of the operation and the consumption of startup fuel) by numerical experiment on a specially developed model. The stage of loading a portion of startup fuel in the fluidized bed heated to 460-680 K and the subsequent fuel burnup is analyzed here.

Analysis of the experimental data obtained on a 20-kW laboratory boiler [4] and on an 8-MW experimental commercial boiler [3] allows the following simplifying assumptions to be made in modeling the given process: the hydrodynamics of the apparatus with respect to the solid phase is described by an ideal-mixing model; the change in mass of the fluidized bed in the startup period is determined solely by the consumption of the component which is burning up; the volume of exhaust gases is equal to the volume of air supplied; the mean diameter of the bed particles in the startup period remains constant; and the only combustion products are H_2O and CO_2 .

Taking account of these assumptions, the mathematical model describing the startup of the fluidized-bed equipment in the case of an exothermal reaction is written as follows.

The balance of solid material is determined by the coal burnup in the bed and the loss by entrainment

$$dM_{\rm c}/dt = -KM_{\rm c} - K(\bar{d})M_{\rm c}.$$
(1)

Institute of Chemistry and Chemical Technology, Siberian Branch, Academy of Sciences of the USSR, Krasnoyarsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 59, No. 1, pp. 126-131, July, 1990. Original article submitted May 24, 1989.

923