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Generalized Correlation for the Physical and Psychometric Properties of Chlorodifluromethane

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Abstract

Chlorodifluoromethane is used as pure or in mixture for refrigeration (medium-high temperatures). It is also used as a blowing agent for extruded polystyrene and polyurethane foams and a component in sterilant gas mixtures. Anew generalized correlation for the physical and psychometric properties of liquid Chlorodifluromethane as a function to temperature are introduced, Equation (1). The new correlation was statistically compared with those previously presented and found to be:

$$\text{Property} = A + BT + CT^2 + DT^3 \quad \ldots(1)$$

Where
A, B, C and D are the property constants,
T is the temperature in degrees centigrade.

Keywords

Physical and psychometric properties, Chlorodifluromethane

Introduction

Chlorodifluoromethane is a non-flammable, colorless and nearly odorless gas under normal conditions. A large proportion is used as a chemical intermediate and therefore not emitted into the atmosphere. Other important uses are in refrigeration and in air conditioning systems; with present practice, most of the chlorodifluoromethane so used will eventually be emitted into the atmosphere[3].Its moderate water solubility and low octane/water partition coefficient indicate a negligible bioaccumulation potential. Contamination of water and food would not be expected from its physical and chemical properties and has not been reported.

Chlorodifluromethane, CHF_2Cl is rapidly becoming the most important halogenated refrigeration coolant and industrial solvent replacing coolants and solvents that have been restricted because of environmental reasons or toxicity. Chlorodifluoromethane was used as an alternative to the highly ozone-depleting CFC-11 and CFC-12, because of its relatively low ozone depletion potential of 0.055.The withdrawal of fluorocarbons as aerosol propellants, refrigeration coolants and polyurethane foam blowing agents due to environmental reasons and the restrictions on the use of many solvents due to their toxicity or flammability resulted in the recent widespread use of Chlorodifluromethane in many major fields as an excellent replacement due to its acceptance by human and environment, since it is the least toxic of the common industrial refrigerant, the least effect on atmospheric ozone layer among. In this work, and due to the extreme importance of the physical and psychometric properties and their variation with temperature in assigning Chlorodifluromethane of a certain application, a new generalized correlation for the physical and psychometric properties of Chlorodifluromethane as function to temperature is introduced. Also, a literature survey on these physical and psychometric properties and their correlations as functions of temperature that previously introduced are included and a statistical comparison among the new correlation and previous correlations is established.

Literature Survey

Chlorodifluromethane is a clear, colorless, volatile liquid with a mild ethereal odor. Though only slightly soluble in water, it is completely miscible with other chlorinated solvents. Chlorodifluromethane (CHF_2Cl) is nonflammable and nonexplosive[4].

Many authors published several physical and psychometric properties of Chlorodifluromethane as single temperature properties or as temperature dependent properties. The most important physical properties of Chlorodifluromethane as a single temperature properties can be summarized by density, Specific heat capacity, Thermal conductivity and Kinematic Viscosity.

Many authors [4,5,6,9,10,11] presented several Chlorodifluromethane physical properties as temperature dependent properties. In the forms of data tables, graphical correlations and mathematical correlations.

The Dupont Chemical Co. [1] published a data table of Chlorodifluromethane chemical and physical properties versus temperature, Table (1).

Coluson and Richardson [8] presented correlations for Chlorodifluromethane viscosity

and vapor pressure, Equations (2 and 3), respectively.

$$\log(\mu) = 359.55\left(\left(\frac{1}{T}\right) - \frac{1}{225.13}\right) \ldots (2)$$

$$\text{For } -44 \text{ K to } 59 \text{ K} \quad \ln(P) = 16.3029 - \frac{2622.44}{(T - 41.70)} \quad \ldots. (3)$$

Where μ in mN.s / m^2, P in mm Hg and T in K.

Cheric[3] presented vapor pressure correlation for liquid Chlorodifluromethane as a function to temperature, Equation (4).

$$\ln p = \ln\left(\frac{743}{101.325}\right) - 101.08632 \ln(T + 273.15) - \frac{4430.610}{T + 273.15} + 83.7786 + 9.812512 \times 10^{-6}(T + 273.15)^2 \quad \ldots(4)$$

Where P in mmHg and T in ◦C.

Mallu and Rao[6] introduced a graphical monograph correlation for the thermal conductivity of liquid Chlorodifluromethane as a function of temperature, Figure (1).

Perry and Chilton [5] introduced a graphical correlation as a monograph relating the liquid Chlorodifluromethane heat capacity to temperature in two units axes, Figure (2).

Gallant [10] presented graphical correlations for Chlorodifluromethane heat capacity, liquid density, liquid thermal conductivity and liquid viscosity, Figures (3 - 6), respectively. These graphical correlations had same temperature ranges as indicated in each figure.

Ashrae [11] presented a published a table for the values of heat capacity, liquid density, liquid viscosity and liquid thermal conductivity as functions to temperature, Table (2).

The Correlation coefficient is a statistical dimensionless quantity, demonstrate how data tends to be represented by a certain fitted equation. This quantity is defined by Equation (5) and its value lies between 0 and 1. As the correlation coefficient approaches unity, the fitted equation approaches perfection [12].

$$r = \sqrt{\frac{\sum_{i=1}^{n}(Y_{i,es.} - \bar{Y})^2}{\sum_{i=1}^{n}(Y_{i.} - \bar{Y})^2}} \quad \ldots\ldots(5)$$

Where

$$\bar{Y} = \frac{\sum_{i=1}^{n} Y_i}{n} \quad \ldots\ldots.(6)$$

Y_i =Calculated value by other correlation equation. (eqn.1)

$Y_{i,es}$=Estimated statistical calculated by new correlation. (Table.3)

The standard error of estimate is statistical measure of the scatter about the regression curve of Y on X, presented by Equation (7) [12].

$$S = \sqrt{\frac{\sum_{i=1}^{n}(Y - Y_{es.})^2}{n}} \quad \ldots..(7)$$

Results:

The data used to formulate the new correlation were those of Ashrae[11]. The original data were in British units which were converted to SI system.

The General correlation calculations were made using the least square method is.

$$\Pi = \sum_{i=1}^{n} \lfloor y_i - f(x_i) \rfloor^2 = \sum_{i=1}^{n} \lfloor y_i - (a_o + a_1 x_i + a_2 x_i^2 + a_m x_i^m) \rfloor^2 = min \ldots..(8)$$

$$\frac{\partial \Pi}{\partial a_i} = 2\sum_{i}^{n} \lfloor y_i - (a_0 + a_1 x_i + a_2 x_i^2 + \cdots . + a_m x_i^m) \rfloor = 0 \ldots(9)$$

For density property ρ equ.(8) can be written as following:

$$\Pi = \sum_{i=1}^{i=4} (\rho_i - T_i)^2 = \sum_{i=1}^{4} \rho_i - (A + BT_i + CT_i^2 + DT_i^3)^2 = \min \quad \ldots.(10)$$

To obtain the least square error, the unknown coefficients A, B, C and D must yield zero first derivatives. Approximation of the constant A,B,C and D for any given set of four points data,(ρ_1,T_1),(ρ_2,T_2),(ρ_3,T_3) and (ρ_4,T_4) where n=3+1=4 ,eqn. (9)& (10) can be applied as following:

$$\frac{\partial \Pi}{\partial A} = 2\sum_{i=1}^{i=4} \lfloor \rho_i - (A + BT_i + CT_i^2 + DT_i^3) \rfloor = 0 \quad \ldots.(11)$$

$$\frac{\partial \Pi}{\partial B} = 2\sum_{i=1}^{i=4} T_i \lfloor \rho_i - (A + BT_i + CT_i^2 + DT_i^3) \rfloor = 0 \quad \ldots..(12)$$

$$\frac{\partial \Pi}{\partial C} = 2\sum_{i=1}^{i=4} T_i^2 \lfloor \rho_i - (A + BT_i + CT_i^2 + DT_i^3) \rfloor = 0 \quad ..(13)$$

$$\frac{\partial \Pi}{\partial \mathrm{D}} = 2\sum_{i=1}^{i=4} {T_i}^3 \left[\rho_i - \left(\mathrm{A} + \mathrm{B}T_i + \mathrm{C}{T_i}^2 + \mathrm{D}{T_i}^3\right)\right] = 0 \quad \ldots(14)$$

The unknown coefficients A, B, C and D can hence be obtained by solving the above linear equations. For other properties the same procedure can be applied. A software called "STATISTICA" can be applied same results be achieved.

The new correlation introduced in this work is seen in Equation (1) and correlation constants for each data property are listed in Table (3).

Discussion:

This comparison was made in terms of correlation coefficient, standard error of estimate and equation complexity.

The new correlation standard error of estimate and correlation coefficient for each property and those of the previous presented correlations were estimated using Equations (5 to 7) for the same temperature range. In order to compare among each property of the new correlation and those of the previous correlations, results of the correlation coefficient and standard error of estimate of each correlation are arranged in Table (4).

The criteria used to decide the best correlation was that both the correlation coefficient must approaches unity (best fitted function) and the standard error of estimate must approaches zero (the least scatter), simultaneously. Mathematically, by using the simple optimization equation or Rosenbrock function [12] which measures the sum of deviation from optimum value of both correlation coefficient (1) and standard error of estimate (0), simultaneously, the above criteria was written as

Optimized function = $(1\text{-}r)^2+(0\text{-}s)^2 = (1\text{-}r)^2+s^2$ …(15)

Where r is the correlation coefficient and s is the standard error of estimate.

As seen in Table (3), the optimized function value of the new correlation was smaller (minimum) for viscosity which clearly indicates that the new correlation is superior to any other correlation. Yet, the new correlation of less complexity, more simple to memorize, gathering five properties in one equation and easiest to program on a computer.

The first advantage of the new correlation and the previous mathematical correlations over those graphically based correlations is accuracy. With a graphical correlation, usually a monograph, points in several scales have to be located, with a possibility for error each time. Then, if a pencil line is drawn, there is an error because of the width of the trace; or, if a ruler is used, a parallelism error is involved. Also, there is frequently a multiplying effect of these errors, due to the geometry of the system.

Another advantageous use of mathematical equations is in the solution of problems that normally requires trial-and-error calculations.

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معادلة جديدة عامة للخواص الفيزيائية والثرموديناميكية لكلورودايفلوروميثين

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الخلاصة:

يعتبر كلورودايفلوروميثين من المركبات الرئيسية المستخدمة كسوائل لعملية التبر يد بشكل منفصل او كجزء من سوائل التبريد الاخرى.كما انه يستخدم كعامل مساعد لعمليات البثق للصفائح الرغوية لمركبات البوليستايرين ومركبات البولييوراثين السائلكما ان له استخدامات مختلفة اخرى ، لقد تم تقديم معادلة جديدة عامة للخواص الفيزيائية و الثرموداينميكة لكلورودايفلوروميثين كدالة لدرجة الحرارة, معادلة رقم (1). كما تمت مقارنة المعادلة الجديدة مع المعادلات المعروفة والمستخدمة وقد تبين ان نتائج معادلتنا تتوافق مع نتائج المعادلات الاخرى بشكل

الخاصية = $A + BT + CT^2 + DT^3$ ...(1)

حيث

A, B, C, D هي ثوابت الخاصية.

T هي درجة الحرارة المئوية.

APPENDIX A

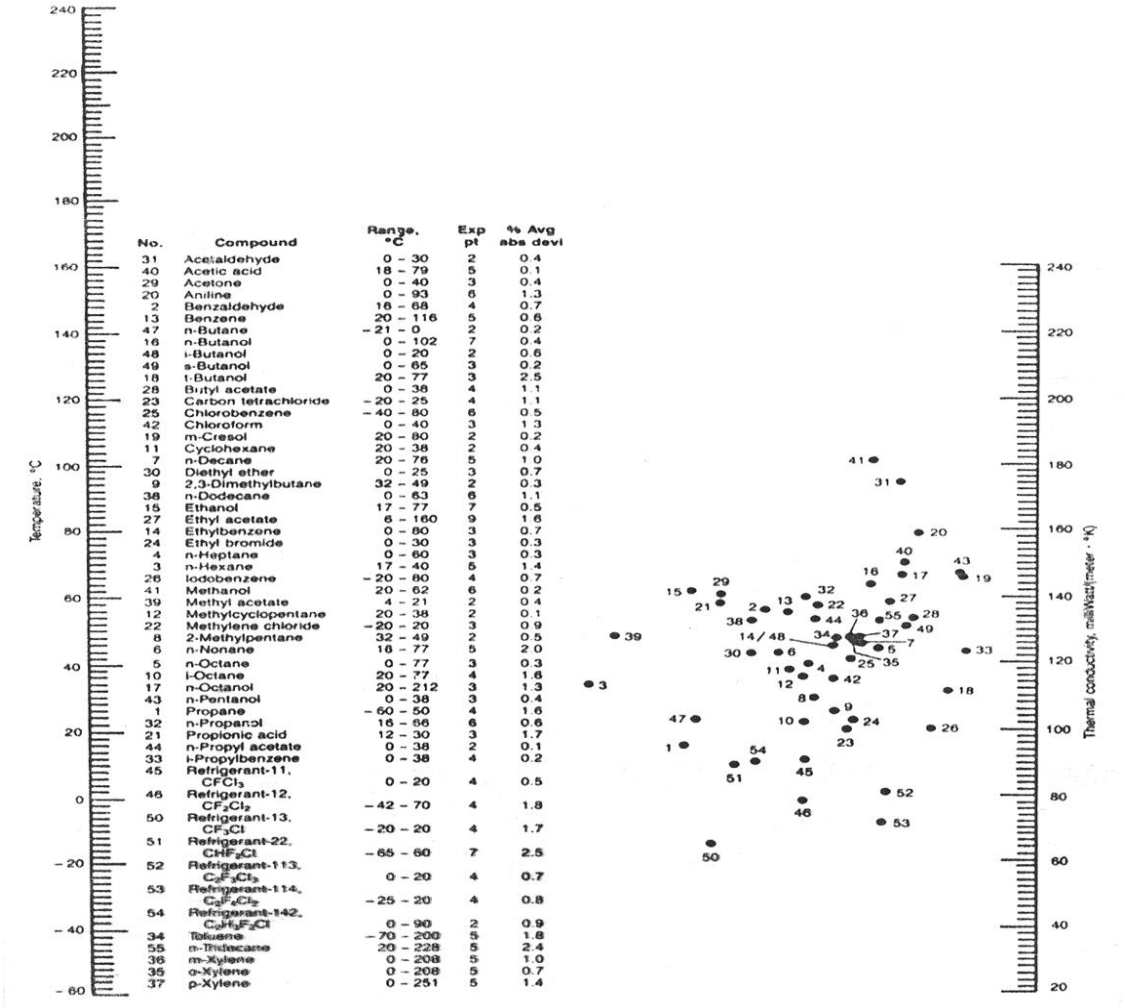
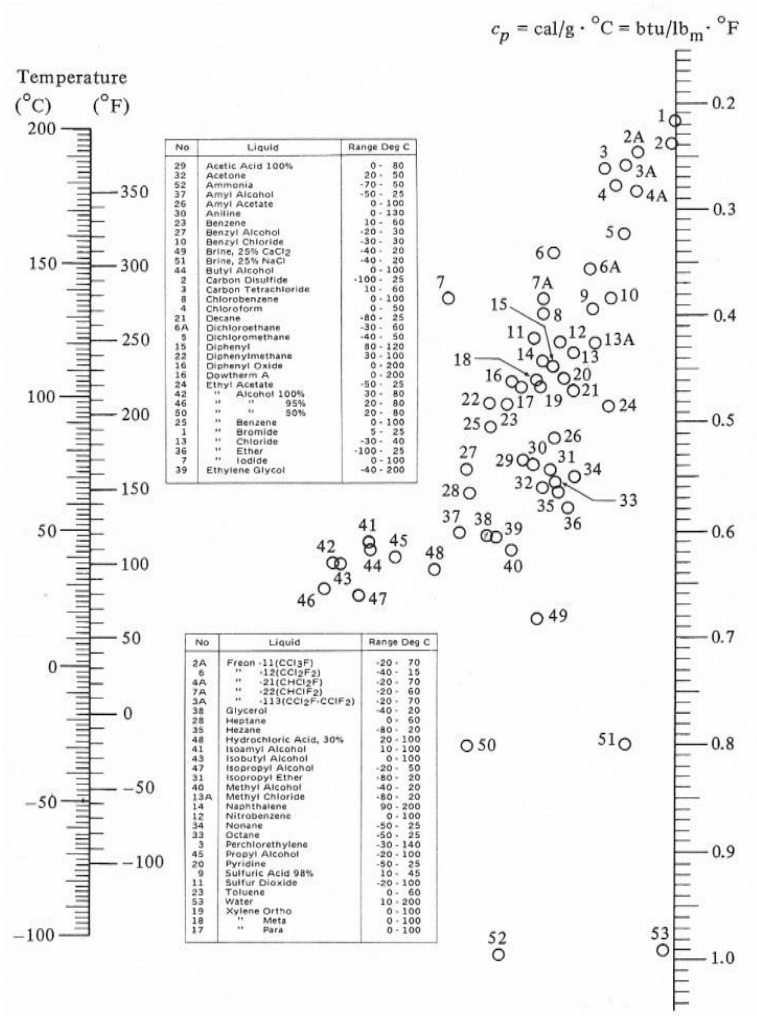


Figure (1): Estimating thermal conductivity of Chlorodifluromethane (point no. 51) [1].



No	Liquid	Range Deg C
29	Acetic Acid 100%	0 - 80
32	Acetone	20 - 50
52	Ammonia	-70 - 50
37	Amyl Alcohol	-50 - 25
26	Amyl Acetate	0 - 100
30	Aniline	0 - 130
23	Benzene	10 - 60
27	Benzyl Alcohol	-20 - 30
10	Benzyl Chloride	-30 - 30
49	Brine, 25% $CaCl_2$	-40 - 20
51	Brine, 25% NaCl	-40 - 20
44	Butyl Alcohol	0 - 100
2	Carbon Disulfide	-100 - 25
3	Carbon Tetrachloride	10 - 60
8	Chlorobenzene	0 - 100
4	Chloroform	0 - 50
21	Decane	-80 - 25
6A	Dichloroethane	-30 - 60
5	Dichloromethane	-40 - 50
15	Diphenyl	80 - 120
22	Diphenylmethane	30 - 100
16	Diphenyl Oxide	0 - 200
16	Dowtherm A	0 - 200
24	Ethyl Acetate	-50 - 25
42	" Alcohol 100%	30 - 80
46	" " 95%	20 - 80
50	" " 50%	20 - 80
25	" Benzene	0 - 100
1	" Bromide	5 - 25
13	" Chloride	-30 - 40
36	" Ether	-100 - 25
7	" Iodide	0 - 100
39	Ethylene Glycol	-40 - 200

No	Liquid	Range Deg C
2A	Freon -11(CCl_3F)	-20 - 70
6	" -12(CCl_2F_2)	-40 - 15
4A	" -21($CHCl_2F$)	-20 - 70
7A	" -22($CHClF_2$)	-20 - 60
3A	" -113(CCl_2F-$CClF_2$)	-20 - 70
38	Glycerol	-40 - 20
28	Heptane	0 - 60
35	Hexane	-80 - 20
48	Hydrochloric Acid, 30%	20 - 100
41	Isoamyl Alcohol	10 - 100
43	Isobutyl Alcohol	0 - 100
47	Isopropyl Alcohol	-20 - 50
31	Isopropyl Ether	-80 - 20
40	Methyl Alcohol	-40 - 20
13A	Methyl Chloride	-80 - 20
14	Naphthalene	90 - 200
12	Nitrobenzene	0 - 100
34	Nonane	-50 - 25
33	Octane	-50 - 25
3	Perchlorethylene	-30 - 140
45	Propyl Alcohol	-20 - 100
20	Pyridine	-50 - 25
9	Sulfuric Acid 98%	10 - 45
11	Sulfur Dioxide	-20 - 100
23	Toluene	0 - 60
53	Water	10 - 200
19	Xylene Ortho	0 - 100
18	" Meta	0 - 100
17	" Para	0 - 100

Figure (2): Heat capacity of Chlorodifluromethane (point no. 7A) [3]

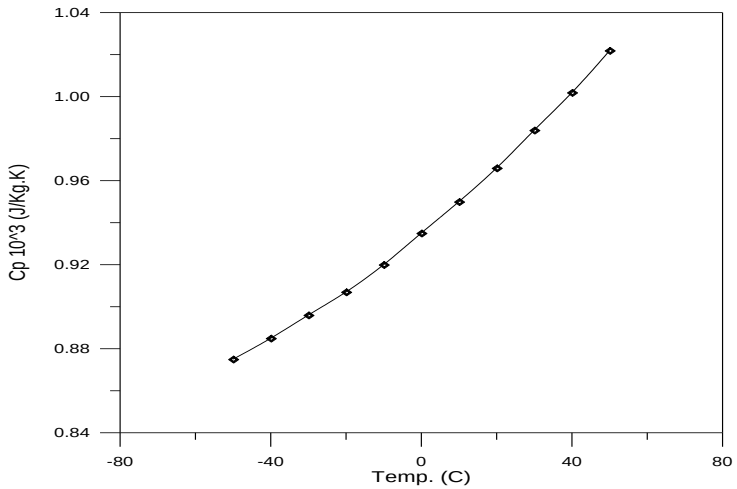


Figure (3): The heat capacity of Chlorodifluromethane over a range -80 °C to 80 °C.

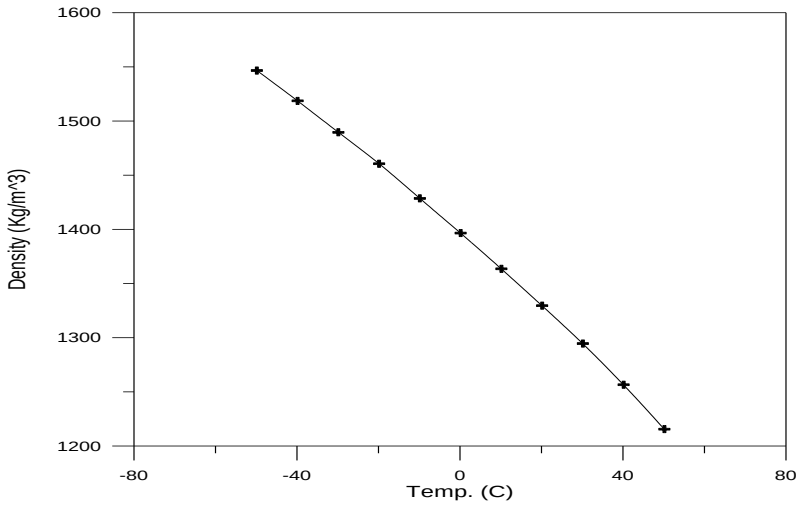


Figure (4): The liquid density of Chlorodifluromethane over a range -80 °C to 80 °C.

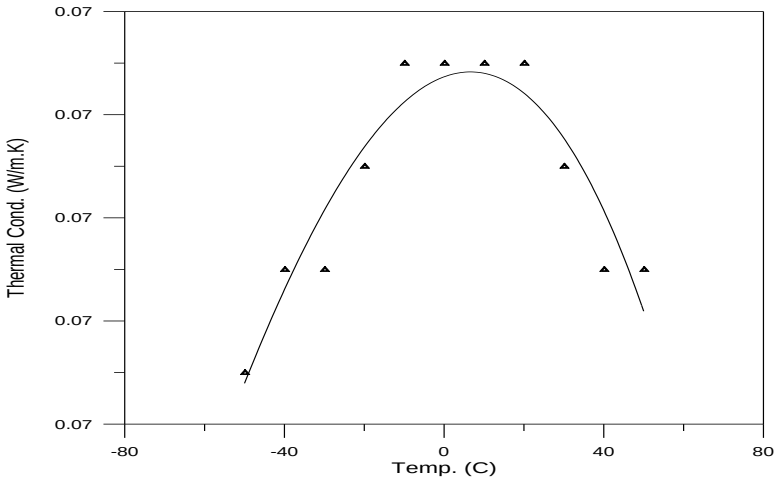


Figure (5): Liquid thermal conductivity of Chlorodifluromethane over a range -80°Cto 80°C.

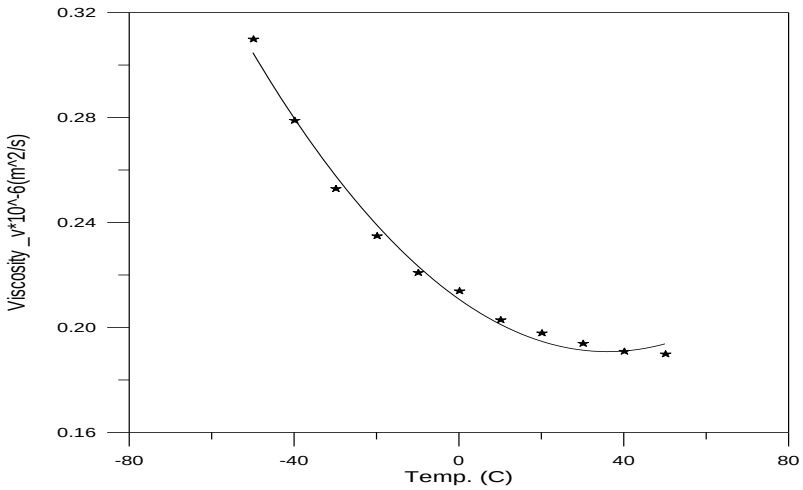


Figure (6): The Liquid viscosity of Chlorodifluromethane over a range -80 °C to 80 °C

APPENDIX B

Table (1): some physical data of Chlorodifluromethane

General Specifications

Appearance: Liquefied gas
Physical State: Gas at normal temperatures
Molecular Weight: 94.4
Chemical Formula: CHClF2 (wt%) = 53
Odor: Slightly ethereal
pH: Neutral
Boiling Point: -33°C (-30.5°F) Average
Melting Point: Unknown
Vapor Pressure: 111.2 psia @ 25°C (77°F)
Vapor Density: 3.5 (Air = 1.0)
Evaporation Rate: Greater than 1 Compared to: CCl4 = 1.0
% Volatiles: % Volatiles by volume @ 68°F (20°C) = 100
Flash Point: None detected; will not burn

Liquid phase

Liquid density (1.013 bar at boiling point) : 1413 kg/m^3
Liquid/gas equivalent (1.013 bar and 15 °C (59 °F)) : 385 vol/vol
Boiling point (1.013 bar) : -40.8 °C
Latent heat of vaporization (1.013 bar at boiling point) : 233.95 kJ/kg

Critical point

Critical temperature : 96 °C
Critical pressure : 49.36 bar

Gaseous phase

Gas density (1.013 bar at boiling point) : 4.706 kg/m^3
Gas density (1.013 bar and 15 °C (59 °F)) : 3.66 kg/m^3
Compressibility Factor (Z) (1.013 bar and 15 °C (59 °F)) : 0.9831
Specific gravity (air = 1) (1.013 bar and 21 °C (70 °F)) : 3.08
Specific volume (1.013 bar and 21 °C (70 °F)) : 0.275 m^3/kg
Heat capacity at constant pressure (Cp) (1.013 bar and 30 °C (86 °F)) : 0.057 kJ/(mol.K)
Heat capacity at constant volume (Cv) (1.013 bar and 30 °C (86 °F)) : 0.048 kJ/(mol.K)Ratio of specific heats (:Cp/Cv) (1.013 bar and 30 °C (86 °F)) : 1.178253
Viscosity (1.013 bar and 0 °C (32 °F)) : 0.0001256 Poise

Miscellaneous

Solubility in water (1 bar and 25 °C (77 °F)) : 0.7799 vol/vol

Table (2): chemical and physical properties versus temperature of Chlorodifluromethane

Temperature - T -(^{o}C)	Density - ρ -(kg/m^3)	Specific Heat Capacity - c_p -(10^3 J/kg.K)	Thermal Conductivity - k -(W/m K)	Kinematic Viscosity - ν -(10^{-6} m^2/s)	Prandtl Number - Pr -
-50	1547	0.875	0.067	0.310	6.2
-40	1519	0.885	0.069	0.279	5.4
-30	1490	0.896	0.069	0.253	4.8
-20	1461	0.907	0.071	0.235	4.4
-10	1429	0.920	0.073	0.221	4.0
0	1397	0.935	0.073	0.214	3.8
10	1364	0.950	0.073	0.203	3.6
20	1330	0.966	0.073	0.198	3.5
30	1295	0.984	0.071	0.194	3.5
40	1257	1.002	0.069	0.191	3.5
50	1216	1.022	0.069	0.190	3.5

Table (3): physical properties of Chlorodifluromethane as single temperature properties**.**

Property	A	B	C	D
Density, kg/m^3	1862.13920	- 2.9912703	0.006273	-6.5X10^{-6}
Heat capacity, KJ/kg.K	1.61279672	- 0.00551354	0.00001811	-2X10^{-8}
Thermal conductivity, W/m.K	0.321	- 0.001	2.1 X10^{-6}	-2X10^{-8}
Viscosity, N.m/s^2	0.023211561	- 0.000216921	66.28X10^{-7}	-7X10^{-9}

Table (4): Statistical Comparison among the new correlation and those previously presented**.**

Property	Correlation coefficient	Standard error of estimate	Optimized function
Density	0.988558	3.411482	_
Heat capacity	0.997911	0.041171	_
Thermal conductivity	0.991900	0.0117771	_
Viscosity	0.979300	0.000366	0.000000522
	0.349579	0.000029	0.433780