PART - A.

CHAPTER - 3

CRITICAL PROPERTIES

Chapter - 3.

CRITICAL PROPERTIES*.

3.1 Abstract:

The critical properties of Freon refrigerants are very important for estimating their limits of performance. Many theoretical methods have been advanced by different scientists to estimate the critical properties of various chemical compounds but no thorough study appears to have been done in respect of Freon refrigerants. In this chapter the critical properties of most of these refrigerants have been calculated theoretically. These values have been compared with published experimental data. Indications have been given as to which theoretical method appears to give best results for Freon refrigerants. Unpublished critical properties have been estimated and tabulated.

3.2 Introduction:

Theoretical estimation of physical, chemical and thermodynamic properties of Freon refrigerants is necessary as the estimated values will give the refrigeration engineer an idea of the performance of his plants even when experimental values are not known. The critical pressure, Critical temperature and critical volume are very important for estimating the limits of performance of refrigerating machines and Freon turbines (Freon turbines have been described in part B of this thesis).

---

*A paper on this subject was published in April, 1970 in CLIMATE CONTROL. Unfortunately, no reprints are available.

Estimated values of critical properties are also required for experimental scientists to have prelimnary idea about the ranges of equipments required to determine the critical values experimentally. It has been shown by Hirschfelder, Curtiss & Bird[17] and many other scientists that accurate experimental determination of critical properties is difficult. Theoretical estimations of critical properties are therefore, essentially required for all scientists. Badylkes[46] has also recommended theoretical estimation of critical properties for halogenated refrigerants, in the absence of experimental data.

In this chapter the critical properties of most of the Freon refrigerants developed so far[18], have been calculated theoretically and the values have been compared with available experimental data.

Many theoretical methods for estimating the critical properties of liquids and gases have been developed. Reid and Sherwood[19] have critically analysed them and have generally recommended methods to be used for different compounds. In this chapter, only such methods have been utilised which yield results very close to available experimental values. It has been assumed that these methods will also give satisfactory results in the case of refrigerants where experimental data are not available.

3.3. Critical Temperature:

Three well known methods have been used to find critical temperatures. All the three methods are modification of the Guldberg rule which states that the critical temperature of

of any substance is 1.5 time its normal boiling temperature, both temperatures being taken in absolute units.

(a) Vowles's method [19]

$$T_c = \frac{T_b}{\theta} \qquad \ldots\ldots (3.1)$$

(b) Reidel's method [19]

$$T_c = \frac{T_b}{\theta} \qquad \ldots\ldots (3.2)$$

where $\theta = 0.574 + \Sigma \Delta T$

(c) Lydersen's method [20]

$$T_c = \frac{T_b}{\theta} \qquad \ldots\ldots (3.3)$$

where $\theta = 0.567 + \Sigma \Delta T - (\Sigma \Delta T)^2$

T_c = Critical temperature, ^oK

T_b = Normal boiling point, ^oK

θ = Constant, different for each compound which may be calculated by summing atomic and structural constants representing the component parts of the molecule.

Values of ΔT required for calculating 'θ' as available from references [19,20] have been reproduced at Appendix No.1. Values of T_b have been taken from reference [18]. Experimental values of T_c have also been taken from reference [18].

Theoretically calculated values of T_c based on the above three methods and the percentage of error have been given in Table No. 3.1.

Recommendation:-

The average of the values obtained by both Riedel's and Lydersen's methods is recommended for use.

3.4 Critical Pressure

In this case also three methods advanced by the previous three authors have been used to calculate the critical pressures of Freon refrigerants.

(a) Vowles's method [19]

$$P_c^{0.8} = \frac{T_c}{\gamma} \qquad \ldots\ (3.4)$$

(b) Riedel's method [19]

$$P_c = \frac{M}{(\emptyset + 0.33)^2} \qquad \ldots\ (3.5)$$

(c) Lydersen's method [20]

$$P_c = \frac{M}{(\emptyset + 0.34)^2} \qquad \ldots\ (3.6)$$

where,

P_c = Critical pressure in atmospheres

M = Molecular weight

and $\emptyset$ = To be calculated by adding the atomic and structural constants as given in References [19] and [20] and reproduced in Appendix No. 1.

T_c = Critical temperature in degrees Kelvin.

Theoretically calculated values of P_c based on the above three methods and the percentage of errors have been given in table No. 3.2.

Recommendations :-

The average of the values obtained by both Riedel's

and Lydersen's method is recommended for use.

3.5 Critical Volume:

Critical Volumes have been estimated by summing incremental constants representing various atoms or atomic configurations. Vowles's [19] and Lydersen's [20] methods have been used and the results are given in the table No. 3.3. The incremental constants of different atoms have been given in Appendix No.1.

Recommendation:-

The average of the values obtained by both Vowles's and Lydersen's methods is recommended for use.

All critical values of one sample refrigerant has been worked out in the appendix No.2 at the end of the 1st part of the thesis.

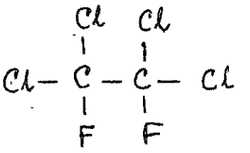
3.6 Conclusion:

(a) A consolidated table of critical properties of Freon refrigerants based on the values of table Nos.1,2 and 3 has been given in table No.3.4. This will be very useful for refrigeration engineers.

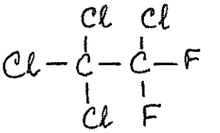
(b) These methods will obviously give same critical property values for all refrigerants having the same number of Carbon, Fluorine and Chlorine atoms. Sometimes different refrigerants are formed having the same number of Carbon, Fluorine and Chlorine atoms bonded differently. Two pairs of such refrigerants are F 112, F 112_a and F 114, F 114_a.

Their chemical formulae are as follows:-

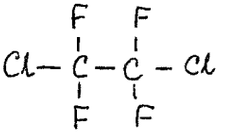
F 112 - Tetrachlorodifluoro ethane
(C Cl_2F CCl_2F)



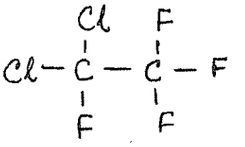
F 11 2_a - Tetrachloro - difluoro ethane
(CCl_3 $CClF_2$)



F 114 - Dichlorotetra fluoro ethane
($CClF_2$ $CClF_2$)



F 114_a - Dichlorotetra fluoro ethane
(C Cl_2F CF_3)



The critical temperature and critical pressure values of F 114 and F 114_a as published in Reference No. [18] are found to be almost equal. This proves the validity of the theoretical methods described in this chapter.

****