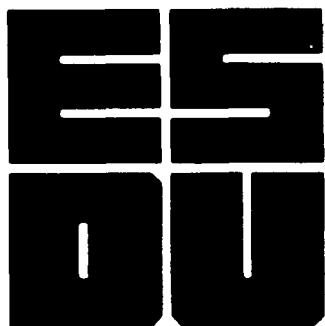


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Engineering Sciences Data

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The evaluation of Chebyshev series used for the representation of vapour pressures

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CHEMICAL ENGINEERING SERIES

PHYSICAL DATA SUB-SERIES

ITEM No.PD1

The need for accurate values of physical properties of fluids arises in connection with a wide range of aeronautical, chemical and mechanical engineering design problems involving, for example, heat exchangers, piping networks, distillation columns, and so on. Although the final equipment may be of many diverse types, the data required are common to all and the Physical Data Sub-series was established to provide a source of such accurate values obtained by a critical evaluation of published and available unpublished information. With the use of computer design programs into which physical data values have to be fed there is a need also to provide equations from which values can be generated as required, in addition to tabular and graphical presentations. These are included whenever practicable in the individual Data Items and in the case of the vapour pressure group of Items the equations are in the form of Chebyshev polynomials. To assist users of these Items who have no experience in the use of this mathematical technique, this guide has been prepared by the Staff of ESDU monitored by the Physical Data and Reaction Kinetics Committee which has the following constitution:

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Mr C.F.Beaton — B.P. Chemicals International Ltd

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The members of staff of the Engineering Sciences Data Unit concerned are:

Mr N.Thompson — Head of Fluid Mechanics and Physical Properties Group

Mr J.Walton — Fluid Mechanics and Physical Properties Group.

The Physical Data and Reaction Kinetics Committee, which first met in May 1966, has the co-operation of many engineers and scientists in industry, research establishments and universities from who much assistance and information are being received. Particular assistance in the preparation of this Item was received from Dr D.Ambrose of the Division of Chemical Standards, National Physical Laboratory.

THE EVALUATION OF CHEBYSHEV SERIES USED FOR THE REPRESENTATION OF VAPOUR PRESSURES

1. INTRODUCTION

The variation of vapour pressure, p , with temperature, T , may be represented approximately by the equation

$$T \log p = B + AT. \quad (1)$$

This equation, however, is not adequate for the exact representation of accurate values over any considerable range of temperature or pressure and a convenient way of improving the fit is to add terms in $T^2, T^3 \dots T^n$ on the right hand side. Such a power series is ill-conditioned and it is more satisfactory to replace it by a series of Chebyshev polynomials as shown in References 2 and 3. An excellent account of Chebyshev series and their properties will be found in Chapter 8 of Reference 1.

This guide shows the application of Chebyshev series to the representation of vapour pressures and indicates the procedure to be followed by the user who wishes to find values of vapour pressure at given temperatures from the Chebyshev coefficients given in related ESDU Data Items, e.g. Item No. 72028. Such calculations would normally be programmed for a digital computer, since the values obtained from the Tables and interpolation formulae given in the Data Items will be adequate for most purposes unless the values have to be computed in a design program.

Section 2 gives a general description of Chebyshev series. Section 3 outlines their adaptation to the representation of the variation of vapour pressure with temperature and Section 4 gives an example to illustrate the evaluation of pressure at a given temperature. The procedures for the evaluation of dp/dT and of the temperature at a given pressure are shown in ESDU Memorandum No. 9*, Reference 4. This also contains a flow diagram for which a program is available.

Appendix A explains how the Chebyshev coefficients may be modified to give vapour pressures in other than SI Units and contains a useful Table of conversion factors for vapour pressures.

2. NOTES ON CHEBYSHEV POLYNOMIALS

One general equation using Chebyshev polynomials to represent the variation of a dependent variable, y , with the independent variable, x , has the form

$$\begin{aligned} y &= \frac{1}{2}a_0E_0(x) + a_1E_1(x) + a_2E_2(x) + \dots + a_sE_s(x) + \dots + a_nE_n(x) \\ &= \frac{1}{2}a_0E_0(x) + \sum_{s=1}^n a_sE_s(x) \quad (-1 \leq x \leq 1) \end{aligned} \quad (2)$$

where $a_0, a_1, \dots, a_n$ are the Chebyshev coefficients and where $E_s(x) = \cos(s \cos^{-1} x)$ is the Chebyshev polynomial in x of degree s . It follows from this definition (Reference 1) that Chebyshev polynomials are

* ESDU Memoranda are available free upon request.

related by the recurrence equation.

$$E_{s+1}(x) - 2xE_s(x) + E_{s-1} = 0. \quad (3)$$

The first few Chebyshev polynomials are thus

$$\begin{aligned} E_0(x) &= 1, & E_3(x) &= 4x^3 - 3x, \\ E_1(x) &= x, & E_4(x) &= 8x^4 - 8x^2 + 1, \\ E_2(x) &= 2x^2 - 1, & E_5(x) &= 16x^5 - 20x^3 + 5x, \end{aligned}$$

and hence from Equation (3) any polynomial in the series can be calculated from its two predecessors. This characteristic of Chebyshev polynomials makes the series especially suitable for computer programming and the series can also be easily summed and differentiated.

It is to be noted that the trigonometric function defining the Chebyshev polynomial is only a mathematical device for generating the algebraic expressions: neither in fitting nor in evaluation is it ever necessary to evaluate any trigonometric ratios. Furthermore, because of the recurrence relation given, evaluation of the individual polynomials is never required.

To evaluate y at a particular value of x in Equation (2), that is to sum the series on the right hand side, the functions $b_n, b_{n-1}, \dots, b_s, \dots, b_0$ defined by the recurrence relationship

$$b_s = a_s + 2xb_{s+1} - b_{s+2} \quad (4)$$

are evaluated starting with b_n and finishing with b_0 , noting that $b_{n+2} = b_{n+1} = 0$. It may then be shown (see Reference 1) that

$$y = \frac{1}{2}(b_0 - b_2). \quad (5)$$

3. THE VAPOUR PRESSURE EQUATION

3.1 Representation of Vapour Pressures

The values of vapour pressure, p , prepared by the NPL in cooperation with ESDU have been generated by evaluating equations of the form

$$T \log p = \frac{1}{2}a_0 + \sum_{s=1}^n a_s E_s(x) \quad (6)$$

which have been fitted to the data for each compound, T being the thermodynamic temperature. In Equation (6) x is a function of temperature, varying between the limits $+1$ and -1 , defined as

$$x = \frac{2T - (T_{\max} + T_{\min})}{T_{\max} - T_{\min}}, \quad (7)$$

$T_{\max}$ and $T_{\min}$ being two thermodynamic temperatures just above and just below the extreme temperatures of the fitted data.