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COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS
AND STANDARDS

RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF PHYSICOCHEMICAL PROPERTIES

(Recommendations 1977)

EDITOR: E. F. G. HERINGTON

SECTION: TESTING DISTILLATION COLUMNS

COLLATORS: E. BRUNNER, E. F. G. HERINGTON and A. NEWTON

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ABBREVIATIONS AND SYMBOLS

A	$-100\{2x(1-x)\ln[(1-x)/x]\}^{-1}$
$\left.\begin{array}{c} a_0 \\ a_1 \end{array}\right\}$	constants in the equation $\ln\alpha = a_0 + a_1(1-2x)$
B_0	volume of charge put into boiler of a batch column
c_i	initial concentration of involatile component in boiler
c_h	concentration of involatile component in boiler when column is under total reflux
HETP	height equivalent to a theoretical plate
H_0	volume of hold up of column
ln	logarithm to base e
log	logarithm to base 10

N number of theoretical plates

$(N+1)_{max}$ the maximum value of $(N+1)$ that should be evaluated with a given test mixture

$(N+1)_{min}$ the minimum value of $(N+1)$ that should be evaluated with a given test mixture

$(N+1)_{opt}$ the optimum value of $(N+1)$ that can be evaluated with a given test mixture

n_D^{20} refractive index at $20°C$ for the D sodium line

p_1 vapour pressure of pure component 1

p_2 vapour pressure of pure component 2

ppm   parts per million by volume

x mole fraction of the more volatile component in the liquid mixture

x_c mole fraction of the more volatile component of mixture placed in boiler to achieve a mole fraction x in the boiler when the column is under total reflux

y mole fraction of the more volatile component in the vapour. This vapour composition may be that of the vapour in equilibrium with liquid of composition x on a plate or it may be the composition of the vapour in the still head. The meaning should be clear from the context.

α relative volatility ratio sometimes called volatility ratio equal to $[y/(1-y)] / [x/(1-x)]$

ρ^{20} density of liquid at $20°C$

INTRODUCTION

Distillation is the most widely used separation process for the isolation of the components of mixtures. Very large scale distillation columns are employed in industry and small apparatus is often used in the laboratory. Separation in fractional distillation is achieved by the interchange of matter between rising vapour and falling liquid in a countercurrent process. Measurements of the theoretical plate equivalence of distillation equipment are used for the following purposes:-

  (i)   to compare the performance of different column designs and packings,

 (ii)   to compare the separations achieved when distillation equipment is used under various conditions; for example to study the effect of different boil-up rates, distributions of reflux and temperature control facilities on the separation efficiency,

(iii)   to provide data by the aid of which large equipment can be built based on information obtained with small scale apparatus,

 (iv)   to examine the effect of the properties of the mixture on the performance of the equipment.

To facilitate intercomparisons of the performance of distillation equipment the European Working Party on Distillation, Absorption and Extraction published a report in 1969 entitled "Recommended Test Mixtures for Distillation Columns" edited by F. J. Zuiderweg (Ref. 1). The present recommendations owe much to this earlier work but seek to update information, provide necessary details on the purity of the components of the test mixtures and give pertinent data in a form easy to use. Thus the requisite data on vapour-liquid equilibrium are arranged in this report so that two independent workers using the results from the same observations should have no difficulty in arriving at the same calculated number of theoretical plates. The effects of experimental errors in the observations on the derived theoretical plate values have also been examined in some detail.

The performance of a fractionating column is commonly expressed in terms of the number of theoretical plates to which the column is equivalent. The vapour arising from a theoretical plate is in equilibrium with the liquid leaving the plate so that for the computation of plate equivalence it is necessary to have vapour-liquid equilibrium data referring to a series of compositions of mixtures of the components. Experimentally measured vapour-liquid

equilibrium data of this type are subject to error and it is therefore imperative that the goodness of the data be established by thermodynamic consistency tests before the data are used. All the vapour-liquid equilibrium data recommended in this Section satisfy thermodynamic consistency tests; details of the results of the application of consistency tests to the data are available in Ref. 2.

Although the performance of distillation columns is measured by the use of equilibrium data yet the separation in fractional distillation takes place by kinetic processes so that the theoretical plate equivalence of a column depends not only on quantities such as the boil-up rate but also on the properties of the mixture used for the test. The properties of the mixture which have an influence on the separations achieved are average relative volatility, solubilities of the liquid components, densities of the phases, surface tension, viscosity, enthalpy of the components, enthalpy of vaporization, and wetting properties of the components towards the column walls and towards the column packing. For this reason column efficiencies should be determined by the choice of mixtures similar in properties to those for which the column will be used in production. To assist in the choice of a suitable mixture, values of liquid density, viscosity, surface tension, enthalpy of vaporization and heat capacity of the liquid at the boiling temperatures of the components at the pressure listed are given in Table I.

Table 1. Properties of the components of the recommended test mixtures at the boiling temperatures

Mixture		I/1		I/2	
Component		Benzene	Toluene	Benzene	Heptane
	Unit				
Pressure	mbar (h Pa)	1013.25	1013.25	1013.25	1013.25
Boiling Temperature	°C	80.100	110.626	80.100	98.425
Density	kg m^{-3}	813.4	783.2	813.4	613.5
Viscosity	mPa s	0.317	0.247	0.317	0.2105
Surface Tension	mN m^{-1}	21.08	17.7	21.08	12.89
Specific Enthalpy of Vaporization	kJ kg^{-1}	393.8	361.4	393.8	316.3
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.88	2.01	1.88	2.56

Mixture		I/3		I/3	
Component		*trans-*Decalin	*cis-*Decalin	*trans-*Decalin	*cis-*Decalin
	Unit				
Pressure	mbar (h Pa)	133.3	133.3	66.66	66.66
Boiling Temperature	°C	115.899	123.653	97.101	104.637
Density	kg m^{-3}	798.2	819.1	812.5	833.3
Viscosity	mPa s	0.593	0.723	0.714	0.874
Surface Tension	mN m^{-1}	20.52	21.94	22.32	23.61
Specific Enthalpy of Vaporization	kJ kg^{-1}	313.1	322.2	321.2	330.6
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.07	2.11	1.98	2.03

Table I (Continued)

Mixture		I/3		I/3	
Component		*trans*- Decalin	*cis*- Decalin	*trans*- Decalin	*cis*- Decalin
	Unit				
Pressure	mbar (h Pa)	13.33	13.33	6.66	6.66
Boiling Temperature	°C	60.894	67.989	47.821	54.748
Density	kg m^{-3}	839.9	860.8	849.6	870.6
Viscosity	mPa s	1.101	1.407	1.323	1.724
Surface Tension	mN m^{-1}	25.72	26.98	26.88	28.15
Specific Enthalpy of Vaporization	kJ kg^{-1}	338.5	348.7	345.8	356.3
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.81	1.86	1.75	1.81

Mixture		I/4		I/4	
Component		Methyl- cyclohexane	Toluene	Methyl- cyclohexane	Toluene
	Unit				
Pressure	mbar (h Pa)	1013.25	1013.25	533.3	533.3
Boiling Temperature	°C	100.934	110.626	79.646	89.485
Density	kg m^{-3}	698.4	783.2	717.2	802.8
Viscosity	mPa s	0.30	0.247	0.36	0.292
Surface Tension	mN m^{-1}	19.37	17.7	17.1	20.3
Specific Enthalpy of Vaporization	kJ kg^{-1}	317.7	361.4	330.2	374.8
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.223	2.01	2.121	1.93

Mixture		I/4		I/5	
Component		Methyl- cyclohexane	Toluene	Chloro- benzene	Ethyl- benzene
	Unit				
Pressure	mbar (h Pa)	266.6	266.6	1013.25	1013.25
Boiling Temperature	°C	59.599	69.494	131.727	136.187
Density	kg m^{-3}	734.8	821.2	983	760.4
Viscosity	mPa s	0.447	0.347	0.292	0.236
Surface Tension	mN m^{-1}	14.9	22.7	20.5	17.3
Specific Enthalpy of Vaporization	kJ kg^{-1}	341.5	386.9	307.6	337.8
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.029	1.86	1.52	0.468

Table 1 (Continued)

Mixture		I/5		I/5	
Component		Chloro-benzene	Ethyl-benzene	Chloro-benzene	Ethyl-benzene
	Unit				
Pressure	mbar (h Pa)	400	400	66.6	66.6
Boiling Temperature	°C	100.399	104.706	53.486	57.636
Density	kg m^{-3}	1019	790.4	1071	833.6
Viscosity	mPa s	0.370	0.296	0.553	0.445
Surface Tension	mN m^{-1}	24.0	20.1	29.5	24.87
Specific Enthalpy of Vaporization	kJ kg^{-1}	331.4	355.4	349.8	381.4
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.46	0.447	1.39	0.423

Mixture		I/6		I/7	
Component		Benzene	1,2-Dichloro-ethane	2-Methyl-naphthalene	1-Methyl-naphthalene
	Unit				
Pressure	mbar (h Pa)	1013.25	1013.25	133.3	133.3
Boiling Temperature	°C	80.100	83.512	164.679	167.776
Density	kg m^{-3}	813.4	1158	900.6	907.4
Viscosity	mPa s	0.317	0.425	0.419	0.457
Surface Tension	mN m^{-1}	21.08	24.4	23.6	24.3
Specific Enthalpy of Vaporization	kJ kg^{-1}	393.8	324.7	357.6	360.7
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.88	1.38	1.98	2.02

Mixture		I/7		I/7	
Component		2-Methyl-naphthalene	1-Methyl-naphthalene	2-Methyl-naphthalene	1-Methyl-naphthalene
	Unit				
Pressure	mbar (h Pa)	66.66	66.66	13.33	13.33
Boiling Temperature	°C	144.329	147.318	104.851	107.674
Density	kg m^{-3}	914.6	925.2	946.7	956.1
Viscosity	mPa s	0.487	0.541	0.701	0.795
Surface Tension	mN m^{-1}	25.0	26.6	29.3	31.1
Specific Enthalpy of Vaporization	kJ kg^{-1}	366.2	369.6	384.8	389.2
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.92	1.95	1.80	1.83

Mixture		I/7		I/8	
Component		2-Methyl-naphthalene	1-Methyl-naphthalene	Heptane	Methyl-cyclohexane
	Unit				
Pressure	mbar (h Pa)	6.67	6.67	1013.25	1013.25
Boiling Temperature	°C	90.534	93.310	98.425	100.934
Density	kg m^{-3}	959.4	967.0	613.5	698.4
Viscosity	mPa s	0.818	0.933	0.2105	0.30
Surface Tension	mN m^{-1}	30.9	32.7	12.89	14.9
Specific Enthalpy of Vaporization	kJ kg^{-1}	392.6	397.4	316.3	317.7
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	1.76	1.79	2.56	2.223

Table I (Continued)

Mixture		I/9	
Component		p-Xylene	m-Xylene
	Unit		
Pressure	mbar (h Pa)	1013.25	1013.25
Boiling Temperature	°C	138.351	139.104
Density	kg m^{-3}	754.7	759.4
Viscosity	mPa s	0.219	0.216
Surface Tension	mN m^{-1}	16.2	16.6
Specific Enthalpy of Vaporization	kJ kg^{-1}	340.1	345.0
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.11	1.99

Mixture		II/1		II/1	
Component		Methanol	Ethanol	Methanol	Ethanol
	Unit				
Pressure	bar	1.013	1.013	3.040	3.040
Boiling Temperature	°C	64.53	78.23	95.31	109.05
Density	kg m^{-3}	750.2	737.9	718.4	704.8
Viscosity	mPa s	0.328	0.444	0.226	0.285
Surface Tension	mN m^{-1}	18.9	17.4	16.1	14.6
Specific Enthalpy of Vaporization	kJ kg^{-1}	1121.4	842	1043.8	777
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	3.00	3.00	3.44	3.44

Mixture		II/1		II/1	
Component		Methanol	Ethanol	Methanol	Ethanol
	Unit				
Pressure	bar	5.066	5.066	10.13	10.13
Boiling Temperature	°C	111.85	125.72	137.13	151.34
Density	kg m^{-3}	699.5	683.9	666.3	647.0
Viscosity	mPa s	0.187	0.228	0.140	0.165
Surface Tension	mN m^{-1}	14.5	12.8	11.8	10.0
Specific Enthalpy of Vaporization	kJ kg^{-1}	996.0	734	914.5	662
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	3.67	3.71	4.11	4.16

Mixture		II/2		II/2	
Component		Propene	Propane	Propene	Propane
	Unit				
Pressure	bar	5.066	5.066	10.13	10.13
Boiling Temperature	°C	-4.64	2.31	19.82	27.48
Density	kg m^{-3}	552.1	525.8	514.1	488.8
Viscosity	mPa s	0.123	0.1243	0.0965	0.0952
Surface Tension	mN m^{-1}	10.8	9.57	7.70	6.60
Specific Enthalpy of Vaporization	kJ kg^{-1}	385.0	409.4	345.2	334.5
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.33	2.01	2.60	2.71

Table I (Continued)

Mixture		II/2		II/2	
Component		Propene	Propane	Propene	Propane
	Unit				
Pressure	bar	15.20	15.20	22.09	22.09
Boiling Temperature	°C	36.36	44.47	53.35	61.91
Density	kg m^{-3}	485.5	460.1	453.4	423.3
Viscosity	mPa s	0.0810	0.0790	0.0667	0.0637
Surface Tension	mN m^{-1}	5.70	4.68	3.78	2.85
Specific Enthalpy of Vaporization	kJ kg^{-1}	311.9	301.4	267.3	260.9
Specific Heat Capacity of Liquid	kJ kg^{-1} K^{-1}	2.85	3.03	3.30	3.52

The information in these recommendations is arranged in the following manner. The next section sets out the general theory and this is followed by considerations governing the design of tests. The individual data sheets give information on each test mixture and include methods for the analysis of the mixtures and pertinent vapour-liquid equilibrium data. The Appendix supplies information on the effects of errors in the values of the volatility ratios and of the mole fractions; choice of composition for the test mixtures; the minimum, maximum and optimum theoretical plate number for mixtures.

GENERAL THEORY

Batch fractional distillation equipment is normally tested by boiling a binary mixture under total reflux until a steady state has been achieved when samples are withdrawn from the still head and boiler for analysis. Compositions are expressed as mole fractions, the mole fraction of the more volatile component in the vapour being y and in the liquid x. Throughout this report the more volatile component is listed first when the names of the two components are given. If the vapour and liquid refer to one theoretical plate the relative volatility ratio (sometimes referred to as the volatility ratio), α, is defined as follows

$$\alpha = [y/(1-y)] / [x/(1-x)] , \qquad (1)$$

and hence it follows that

$$y = \alpha x/[(\alpha-1)x + 1] . \qquad (2)$$

Fractional distillation is usually carried out so that there is a temperature gradient within the distillation column but with the pressure within the column constant to a first approximation. Thus interest centres on the values of the volatility ratio, α, for liquid mixtures containing different mole fractions of components under the same total pressure. It therefore follows that for many mixtures α is a function of x.

Two methods for recording vapour-liquid equilibria data have been adopted in this report. For a mixture of components with boiling properties that differ only slightly, which has been treated as ideal, a single value of the relative volatility ratio, α, for a given total pressure has been given. This value has been calculated from the ratio of the vapour pressures of the pure components. For such a mixture the number of theoretical plate equivalence of the column, N, can be calculated by the use of the Fenske equation (3),

$$N + 1 = \frac{\ln\{[y/(1-y] / [x/(1-x)]\}}{\ln \alpha} \qquad (3)$$

where y is the mole fraction of the volatile component in the still head and x the mole fraction of the same component in the boiler. Natural logarithms (ln) have been widely used throughout this report but logarithms to the base 10 (log) have also been employed.

A method of tabulation has been used for other mixtures which records the equilibrium x-y data and enables the plate equivalence of a column to be found by simple interpolation followed by the subtraction of two quantities. These tables have been prepared from plate to plate calculations starting with $x = 0.05$ and ending where y first exceeds 0.95. The method of tabulation and the technique for using tables of this kind will be illustrated using the table given under I/2 (benzene-heptane) page 2433. To condense the tables values of x and y for $N+1$ equal to 1, 3, 5, 7 etc have been tabulated although in some tables final values have been inserted for even values of $N + 1$ (see page 2434). For any value of $N+1$ the value of y represents the mole fraction of the more volatile component in the vapour in equilibrium with the liquid containing x mole fraction of the same component; hence the y-x equilibrium diagram can be constructed by plotting values of y against those of x from the table; additional values of y and x for $N+1$ of even number can also be plotted (see below).

The values of x and y for even values of $N+1$ can be written down by inspection; for example the value of x for $N+1 = 4$ from the table on page 2434 is 0.3175 and the value of y is 0.4741; the appropriate value of α, if required, can then be calculated from these values of x and y by the use of Equation (1). The table on page 2434 can be used to derive the plate equivalenc of a column by simple calculation. For example, suppose in a test using mixture I/2 x (the pot composition) was found to be 0.1868 and y (the still head composition) was found to be 0.9238, then from the table on page 2434 $N+1$ for the boiler would equal 3 and $N+1$ for the still head would equal 11. Therefore (11-3) = 8 would equal the plate equivalence of the column. In a real situation the boiler and still head compositions would not coincide exactly with values in the table and therefore it will be necessary to interpolate. The following example shows the procedure using data for mixture I/2 (page 2434).

Example:

        Test mixture I/2 (Benzene + Heptane).

From experiment $x = 0.452$ (boiler mole fraction) ,

                     $y = 0.931$ (still head mole fraction) .

According to the table on page 2434 the experimental value of x lies between $N+1 = 3$ and $N+1 = 5$ and by inspection the values for $N+1$ are written down,

$N+1$	x
3	0.1868
4	0.3175
5	0.4741.

Clearly the value of x lies between $N+1 = 4$ and $N+1 = 5$, and by proportional parts it correspond to

$$N+1 = 4 + \frac{0.452 - 0.3175}{0.4741 - 0.3175} = 4.86 \ .$$

Similarly, it may be seen that the experimental value of y lies between $N+1 = 11$ and $N+1 = 13$, and by inspection the values for $N+1$ are written down,

$N+1$	y
11	0.9238
12	0.9367
13	0.9467.

The value of y lies between $N+1 = 11$ and $N+1 = 12$, and by proportional parts it corresponds to

$$N+1 = 11 + \frac{0.931 - 0.9238}{0.9367 - 0.9238} = 11.56.$$

Therefore the plate equivalence of the column is 11.56 - 4.86 = 6.7 theoretical plates.

The tables of $N+1$, x and y for ideal mixtures where α varies with x have been constructed direct from the Antoine vapour-pressure equations (see as an example mixture I/1, p. 2432). The corres- ponding tables for non-ideal mixtures have been calculated from values of $\ln \alpha$ derived from experimental data expressed as a power series in x; the requisite power series has been obtained by fitting experimental vapour-liquid equilibrium data by the method of least squares.

The boiling points of the pure components are listed on the data sheets for selected pressures, but the equilibrium temperatures of the mixtures have not been recorded because published values are often less accurate than the concentration data and in most instances little use is made of temperature in testing columns.

In bubble-tray fractionating-columns the plate efficiency is defined as the number of theore- tical plates determined in a test distillation divided by the number of actual trays. In packed columns the height equivalent to a theoretical plate (HETP) is obtained by dividing the packed length by the number of theoretical plates.

        DESIGN OF TESTS

The test mixture should be chosen so as not to be too easy nor too difficult to separate. Each data sheet shows the maximum and minimum number of plates that can be determined by the use of the mixture.

A mixture must be chosen such that the expected plate equivalence falls in the range suitable for the mixture. A mixture suitable for testing the column at the pressure required must also, of course, be chosen.

Although in the testing of the plate equivalence of fractionating columns it is not essential to determine the dynamic hold-up of the column yet a knowledge of this quantity assists in the design of the optimum conditions for the evaluation of distillation column performance. The simplest experimental method for the determination of the dynamic (operating) hold-up is to place in the boiler a known volume of a solution containing a small amount of relatively involatile material dissolved in a volatile solvent. The column is then run under total reflux at the desired boil-up rate and samples are taken from the boiler when steady state conditions have been reached. The hold-up of the column, H_o, is calculated by Equation (4) from the volume, B_o, of liquid originally placed in the boiler, c_i, the initial concentration of the involatile component in the boiler and c_h, the concentration of involatile component in the boiler when the column is running under total reflux,

$$H_o = B_o(1 - c_i c_h^{-1}).$$ (4)

Stearic acid determined by titration or α-bromonaphthalene determined by refractometry with heptane as the volatile component have been suggested as suitable mixtures for the measurement of hold-up. Other mixtures may be used provided the additive is of very low volatility and provided it is soluble in the mixture; for example a 10% by weight solution of stearic acid in benzene has been employed. For an example and for the necessary precautions to obtain accurate results see Ref. 3.

In the determination of the plate equivalence of a fractionating column past experience or prior published work will usually provide a guide to the magnitude of the plate equivalence to be expected. Such knowledge will enable a suitable initial composition of the feed charge to be selected for an experiment to determine the theoretical plate equivalence. In the absence of such prior knowledge preliminary experiments may be necessary to choose conditions which will give the best accuracy in results. To obtain the best accuracy when an ideal or near ideal test mixture is employed conditions should be chosen so that the sum of x (boiler composition) and y (still head composition) is unity i.e. x and y are equally disposed about the mole fraction 0.5. To satisfy this condition it is necessary that the charge put into the boiler should have a higher concentration of the more volatile component than the desired value of x under total reflux because some of the volatile component will be in the hold-up (see Appendix for discussion). The appropriate equation to calculate the desired initial mole fraction, x_c, is

$$x_c = x + H_o (0.5-x)/B_o,$$ (5)

where x is the required mole fraction in the boiler when a stationary condition has been achieved under total reflux, and B_o and H_o are the volumes of the test mixture used and of the hold-up respectively.

The following provisos apply to information on Reference Materials (a) the recommended materials have not been checked independently by IUPAC, (b) the quality of material may change with time, (c) the quoted sources of supply may not be exclusive sources because no attempt has been made to seek out all possible alternative sources, (d) IUPAC does not guarantee any material that is recommended.

To ensure that the components of the mixture are pure enough for use in a test mixture it is recommended that the separate components be distilled through the column before the mixture is made. The distillation should be carried out with a high reflux ratio with rejection of head and tail fractions. Only the middle fraction boiling at a steady temperature should be used. Care must be taken to eliminate volatile impurities because if they are present they will accumulate in the still head during the test and lead to erroneous values for the plate equivalence. The purity of the starting materials and the possible accumulation of impurities during distillation can best be studied by gas-liquid chromatography. As the nature of the impurities is often not known the purity of the starting materials and of the liquid and vapour samples during distillation should be investigated by the use of two gas-chromatographic columns with stationary phases of different polarities to ensure that the presence of any impurity should not pass unnoticed. Details for the purification of components are given on the data sheets, where methods recommended for analysis to obtain values of x and y are also presented.

In the past density or refractive index measurements have been used for the analysis of liquid and vapour samples but equations connecting these properties with mole fractions are not given here because it is recommended that the property-composition curve should be determined by the analyst using values obtained from measurements made on his own instruments on synthetic mixtures prepared from samples of the components used in making the test mixture.

Gas chromatography (Refs. 4,5) is being employed to an increasing extent for the analysis of liquid and vapour samples in the testing of columns. Numerous types of equipment are offered by a large number of manufacturers, ranging from simple routine apparatus to complex research equipment connected to a computer. For the quantitative analysis necessary here an apparatus in the average price range with a thermal conductivity detector or a combination of thermal conductivity detector and flame ionization detector is adequate. The peaks can be evaluated advantageously with a simple electronic integrator. With the simple mixtures involved in theoretical plate calculations and employing routine gas-chromatographic analysis with an internal standard and integration evaluation a standard deviation of ± 1% of the mole fraction is attainable in the range 0.05-0.20 mole fraction. The standard deviation may be smaller in a laboratory where comprehensive experience in gas chromatography is available. In well equipped laboratories other analytical methods such as i.r. or u.v. spectroscopy can be used.

In each investigation the effect of analytical errors in the values of x and y on the calculated value of the plate efficiency should be examined by the use of Equation (8) in the Appendix or by the study of the $N+1$, x, y table appropriate to the mixture used.

For many packings the performance of the column expressed as the number of theoretical plates is closely dependent on the boil-up rate so that it is necessary to control and measure the boil-up rate whenever the number of theoretical plates is measured. Every effort must be made to ensure complete condensation at the still head and prevent leakage because even a small loss will reduce the apparent number of plates found (Ref. 6). The prevention of even very small leakages is particularly important if highly efficient columns are being tested.

The column under test must be run under total reflux for sufficient time for equilibrium to be established before samples are taken. The equilibration time will be increased if the number of theoretical plates is increased, if the hold-up is increased, if the boil-up is decreased, if the concentration of more volatile component is decreased and if the boiling temperature difference between the components is decreased (Ref. 6). When a test of plate efficiency is being made the experimenter must confirm that a stationary condition has been achieved by taking a succession of samples at increasing time intervals until no change in composition occurs. However, to avoid taking samples much too early, an equilibrium time amounting to between 1 and 1½ h for every 10 theoretical plates may be allowed in the first instance (Ref. 3)

The data sheets giving details of test mixtures are listed in two sections (I and II) in accordance with the pressures at which their use is suitable and within each section mixtures for testing columns with a small number of plates appear before those mixtures for testing columns with a large number of plates. Threshold limit values, flamable limits and minimum ignition temperatures are listed under the title "Safety"; definitions of these terms and further information about them can be found in Ref. 7.

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1. F. J. Zuiderweg (editor), *Recommended Test Mixtures for Distillation Columns*, European Federation of Chemical Engineering, Working Party on Distillation, Absorption and Extraction, Institution of Chemical Engineers, London (1969).
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I/1

BENZENE + TOLUENE TEST MIXTURE

Intended usage: This test mixture may be used to measure the plate efficiencies of columns equivalent to 1-6 theoretical plates at 1013.25 mbar pressure.

Sources of supply and/or methods of preparation: Samples of these compounds may be purchased from many firms, from some of which high purity grades are available. However, as this mixture can only be used to test columns with a small number of plates, components of the highest purity are usually not essential. Nevertheless the components should undergo a preliminary distillatior before use (see p.2431).

Analysis: Gas chromatography is a convenient method of analysis: the procedure should be checked by the quantitative analysis of synthetic mixtures before the specimens from the distillation experiments are analysed. Examples of columns that have been used are (i) Sil-o-cel 30-50 mesh impregnated with 30% w/w Apiezon N (2 m column at 130 °C with hydrogen as carrier gas); (ii) 10% w/w carbowax 1540 on Chromosorb W (3 m column at 80 °C). Infrared spectroscopy may also be used.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/^\circ$ C are given by the following equations, which yield boiling temperatures of 80.100° C (benzene) and 110.626 °C (toluene) for a pressure of 1013.25 mbar (Ref. 1):

$$\text{Benzene:} \quad \log(p_1/\text{mbar}) = 7.03055 - 1211.033/[(t/^\circ\text{C}) + 220.790] \,,$$

$$\text{Toluene:} \quad \log(p_2/\text{mbar}) = 7.07954 - 1344.800/[(t/^\circ\text{C}) + 219.482] \,.$$

Vapour-liquid equilibrium at 1013.25 mbar: the system is treated as ideal so that

$$\ln \alpha = \ln(p_1/p_2).$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.1107	2.3646	5	0.6395	0.8175	2.5252
3	0.2288	0.4179	2.4196	7	0.9199	0.9674	2.5851

For methods to be used for the calculation of the plate equivalence see p. 2430.

Safety: Benzene is very toxic and the maximum concentration in air should not exceed 10 ppm. The flammable limits in air are given as 1.4-7.1% by volume and the minimum ignition temperature in air is 562 °C.

Toluene is also toxic, and the threshold limit value has been set at 200 ppm. The flammable limits in air are 1.17-7.10% by volume and the minimum ignition temperature in air is 536 °C.

REFERENCE

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

I/2

BENZENE + HEPTANE TEST MIXTURE

Intended usage: This test mixture may be used to measure the plate efficiencies of columns equivalent to 1-13 theoretical plates at 1013.25 mbar pressure.

Sources of supply and/or methods of preparation: These compounds are available from a number of chemical firms but it is essential to purchase high grade materials.

A good commercial grade of benzene can be purified further by shaking portions successively with sulphuric acid until the sample is free from thiophen, then with water, dilute sodium hydroxide and with further portions of water. The benzene sample can then be dried with anhydrous calcium chloride. Further purification can be achieved by fractional freezing but whatever pre-treatments are applied the sample should be distilled before use at a high reflux ratio with rejection of head and tail fractions.

The heptane employed must consist solely of the normal isomer and care should be taken to distil the sample before use and to employ only specimens with the correct density and/or refractive index values. A suitable grade for use in test-mixtures is heptane prepared for engine knock-rating measurements available from supplier (A).

Analysis: Determinations of refractive index (benzene, $n_D^{20} = 1.50112$; heptane, $n_D^{20} = 1.38764$) or of density (benzene, $\rho^{20}/\text{kg m}^{-3} = 879.01$; heptane, $\rho^{20}/\text{kg m}^{-3} = 683.76$) give accurate results. Gas chromatography can be used provided the technique is checked by the quantitative analysis of synthetic mixtures of known composition. For example a 2-m column packed with 10% Carbowax 1540 on Chromosorb W at 80 °C has been employed. Ultraviolet spectroscopy can be used for analysis.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/°C$ are given by the following equations (Ref. 1):

Benzene: $\log(p_1/\text{mbar}) = 7.03055 - 1211.033/[(t/°C) + 220.790]$,

Heptane: $\log(p_2/\text{mbar}) = 7.02167 - 1264.900/[(t/°C) + 216.544]$.

These equations yield boiling temperatures of 80.100 °C (benzene) and 98.425 °C (heptane) for a pressure of 1013.25 mbar.

Vapour–liquid equilibrium at 1013.25 mbar: The system is not ideal and the following equation based on experimental data (Ref.2) was used to represent $\ln \alpha$ as a power series in x,

$\ln \alpha = 0.7555 - 0.2463x - 0.03611x^2 - 0.3780x^3$.

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0996	2.1023	9	0.8503	0.8834	1.3332
3	0.1868	0.3175	2.0254	11	0.9067	0.9238	1.2470
5	0.4741	0.6193	1.8046	13	0.9367	0.9467	1.2002
7	0.7283	0.8017	1.5083	14	0.9467	0.9546	1.1845

For methods for the calculation of the plate equivalence see page 2430. Note that the value of α falls rapidly as x increases and that when $x = 0.9467$ one plate increases the concentration of the volatile component by only 0.0079 in mole fraction. Accurate analyses are therefore required if exact plate values are to be found from still-head compositions in this concentratio range.

Safety: Benzene is very toxic and the maximum concentration in air should not exceed 10 ppm. In air the flammable limits are 1.4-7.1% by volume and the minimum ignition temperature is 562°C

The threshold limit value is 500 ppm for heptane and in air the flammable limits are 1.10-6.70% by volume and the minimum ignition temperature 223 °C.

REFERENCES

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum
      Institute Research Project 44, Thermodynamic Research Center, Texas A & M University,
      College Station, Texas.
2. F. J. Zuiderweg (editor), *Recommended Test Mixtures for Distillation Columns,* European
      Federation of Chemical Engineering, Working Party on Distillation, Absorption and Extrac-
      tion, Institution of Chemical Engineers, London (1969).

I/3

TRANS-DECALIN + CIS-DECALIN TEST MIXTURE

Intended usage: This mixture may be used to measure the theoretical plate efficiencies of column equivalent to 2-22 theoretical plates (pressure 133.3 mbar), 2-20 theoretical plates (pressure 66.66 mbar), 1-16 theoretical plates (pressure 13.33 mbar) and 1-15 theoretical plates (pressure 6.66 mbar).

Sources of supply and/or methods of preparation: Decalin is available commercially as a mixture of the two isomers; materials from different sources show considerable variations in the isomer ratio. Purification by repeated shaking of samples with concentrated sulphuric acid until the acid layer remains only slightly coloured is recommended. The hydrocarbon should then be washed with water, then with dilute sodium hydroxide and then with three portions of water. The product should be dried over calcium chloride or molecular sieve. The material should be fractionally distilled under reduced pressure before use as a test mixture. Decomposition has been reported when the hydrocarbon is distilled at atmospheric pressure.

Analysis: Mixtures can be analysed by gas chromatography; a 3-m column packed with silicone oil DC 200 at 150 °C or a 2-4 m column containing 10% Apiezon L and 1% phosphoric acid on Chromosorb P60-80 mesh with hydrogen as carrier gas at 130 °C and a thermal conductivity detector have been recommended.

The composition of mixtures can be determined very accurately from measurements of density (*trans*-decalin, $\rho^{20}/\text{kg m}^{-3}$ = 896.7; *cis*-decalin, $\rho^{20}/\text{kg m}^{-3}$ = 869.7) or of refractive index (*trans*-decalin, n_D^{20} = 1.46932; *cis*-decalin, n_D^{20} = 1.48098). Analysis by i.r. spectroscopy is also possible (850-950 cm^{-1}). Samples of the pure isomers should be used to calibrate these methods.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/^{\circ}$C are given by the following equations (Ref. 1):

$$trans\text{-Decalin:} \quad \log(p_1/\text{mbar}) = 6.98171 - 1564.683/[\,(t/^{\circ}C) + 206.259\,]\,,$$

$$cis\text{-Decalin:} \quad \log(p_2/\text{mbar}) = 7.00019 - 1594.460/[\,(t/^{\circ}C) + 203.392\,]\,.$$

These equations yield boiling temperatures of 115.899, 97.101, 60.894, 47.821 °C for *trans*-decalin and 123.653, 104.637, 67.989, 54.748 °C for *cis*-decalin at pressures of 133.3, 66.66, 13.33 and 6.66 mbar respectively.

Vapour–liquid equilibrium: the system is treated as ideal so that

$$\ln \alpha = \ln (p_1/p_2).$$

Pressure 133.3 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0641	1.3013	13	0.5590	0.6237	1.3080
3	0.0818	0.1040	1.3017	15	0.6845	0.7397	1.3096
5	0.1313	0.1644	1.3024	17	0.7883	0.8299	1.3109
7	0.2041	0.2505	1.3034	19	0.8649	0.8936	1.3118
9	0.3035	0.3625	1.3047	21	0.9168	0.9353	1.3124
11	0.4260	0.4923	1.3063	23	0.9499	0.9614	1.3128

Pressure 66.66 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0656	1.3344	13	0.6331	0.6986	1.3433
3	0.0857	0.1112	1.3350	15	0.7570	0.8073	1.3451
5	0.1432	0.1825	1.3359	17	0.8494	0.8836	1.3464
7	0.2298	0.2852	1.3373	19	0.9109	0.9323	1.3472
9	0.3481	0.4169	1.3391	21	0.9489	0.9616	1.3477
11	0.4894	0.5624	1.3412				

Pressure 13.33 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0695	1.4186	11	0.6417	0.7193	1.4312
3	0.0958	0.1308	1.4197	13	0.7859	0.8404	1.4339
5	0.1761	0.2330	1.4215	15	0.8831	0.9156	1.4358
7	0.3017	0.3810	1.4242	17	0.9397	0.9572	1.4368
9	0.4674	0.5561	1.4276				

Pressure 6.66 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0713	1.4583	11	0.7039	0.7780	1.4740
3	0.1007	0.1405	1.4596	13	0.8380	0.8842	1.4769
5	0.1927	0.2587	1.4620	15	0.9186	0.9435	1.4786
7	0.3381	0.4281	1.4656	16	0.9435	0.9611	1.4791
9	0.5235	0.6176	1.4699				

Safety: Decalin vapour is irritating to the eyes, nose and throat, and the threshold limit value of 25 ppm has been suggested. The minimum ignition temperature in air is 262 °C.

REFERENCE

1. *Selected Values of Properties of Hydrocarbons and Related Compounds*, American Petroleum
    Institute Research Project 44, Thermodynamic Research Center, Texas A & M University,
    College Station, Texas.

I/4

METHYLCYCLOHEXANE + TOLUENE TEST MIXTURE

Intended usage: This mixture may be used to measure the plate efficiencies of columns equi-
valent to 3-31 theoretical plates (pressure 1013.25 mbar), 3-23 theoretical plates (pressure
533.3 mbar), and 3-24 theoretical plates (pressure 266.6 mbar).

Sources of supply and/or methods of preparation: Methylcyclohexane is available from many
firms. Samples should be purified by washing with concentrated sulphuric acid, sodium
carbonate solution and water. The specimen should be dried with anhydrous calcium chloride
or with molecular sieve and distilled until the properties of the fraction chosen closely
approach those of highly purified samples (see Analysis).

Good grades of toluene are available and specimens should be purified by distillation through
an efficient column at a high reflux ratio. Thus, for example, the use of nitration grade
toluene purified by distillation through a 75-plate column with a high reflux ratio has been
recommended. The physical properties of the specimen used to make the test mixture should be
similar to those of the pure material (see Analysis).

Analysis: The determination of the refractive index of a mixture (methylcyclohexane, n_D^{20} =
1.42312; toluene, n_D^{20} = 1.49693) is very convenient; density measurements can also be used
(methylcyclohexane, ρ^{20}/kg m^{-3} =769.39; toluene, ρ^{20}/kg m^{-3}= 866.96).

Gas chromatography (2-m column packed with 10% by weight of Carbowax 1540 on Chromosorb W at
90 °C) and u.v. spectroscopy can also be employed.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/°$C are given
by the following equations (Ref. 1):

       Methylcyclohexane: $\log(p_1$/mbar$)$ = 6.94790 - 1270.763/[$(t/°$C$)$ + 221.416] ,

       Toluene: $\log(p_2$/mbar$)$ = 7.07954 - 1344.800/[$(t/°$C$)$ + 219.482] .

These equations yield boiling temperatures of 100.934, 79.646, 59.599 °C for methylcyclohexane
and 110.626, 89.485, 69.494 °C for toluene at pressures of 1013.25, 533.3 and 266.6 mbar
respectively.

Vapour-liquid equilibrium: the system is non-ideal; the data used (Ref. 2) are similar to
those previously provided (Ref. 3).

Pressure 1013.25 mbar

The following equation was used to represent $\ln\alpha$ as a power series in x,
$\ln \alpha = 0.4932 - 0.4803 x + 0.0332x^2$.

N+1	x	y	α	N+1	x	y	α
1	0.0500	0.0776	1.5988	19	0.8566	0.8691	1.1120
3	0.1172	0.1706	1.5486	21	0.8802	0.8899	1.1010
5	0.2370	0.3126	1.4641	23	0.8986	0.9064	1.0924
7	0.3913	0.4672	1.3639	25	0.9134	0.9197	1.0857
9	0.5361	0.5962	1.2780	27	0.9254	0.9305	1.0802
11	0.6476	0.6909	1.2166	29	0.9352	0.9395	1.0758
13	0.7275	0.7583	1.1751	31	0.9434	0.9470	1.0721
15	0.7844	0.8066	1.1467	32	0.9470	0.9504	1.0705
17	0.8257	0.8422	1.1267				

Note that the value of α decreases rapidly as the value of x increases so that an error of
0.0034 in x will lead to an error of one plate when N+1 = 32.

Pressure 533.3 mbar

The following equation was used to represent ln α as a power series in x,

$$\ln \alpha = 0.5558 - 0.4865x + 0.0176x^2.$$

N+1	x	y	α	N+1	x	y	α
1	0.0500	0.0822	1.7015	15	0.8491	0.8679	1.1682
3	0.1305	0.1971	1.6366	17	0.8839	0.8974	1.1498
5	0.2801	0.3722	1.5233	19	0.9091	0.9191	1.1366
7	0.4636	0.5469	1.3966	21	0.9278	0.9355	1.1270
9	0.6185	0.6781	1.2990	23	0.9421	0.9480	1.1197
11	0.7269	0.7668	1.2355	24	0.9480	0.9532	1.1168
13	0.7996	0.8266	1.1949				

Again the value of α decreases rapidly as the value of x increases so that an error of 0.0052 in x will produce an error of one plate when $N+1 = 24$.

Pressure 266.6 mbar

The following equation was used to represent ln α as a power series in x,

$$\ln \alpha = 0.6782 - 0.6649x + 0.0397x^2.$$

N+1	x	y	α	N+1	x	y	α
1	0.0500	0.0912	1.9061	15	0.8706	0.8845	1.1382
3	0.1569	0.2485	1.7769	17	0.8963	0.9064	1.1209
5	0.3564	0.4638	1.5625	19	0.9152	0.9229	1.1084
7	0.5581	0.6348	1.3764	21	0.9296	0.9355	1.0990
9	0.6953	0.7427	1.2650	23	0.9408	0.9455	1.0918
11	0.7801	0.8100	1.2016	25	0.9497	0.9535	1.0860
13	0.8342	0.8541	1.1632				

Again the value of α decreases rapidly as the value of x increases so that an error of 0.0038 in x will produce an error of one plate when $N+1 = 25$.

For the method for the calculation of plate equivalence from the above tables see p. 2430.

Safety: The threshold limit value is 500 ppm for methylcyclohexane and in air the lower flammability limit is 1.15% by volume and the minimum ignition temperature is 285 °C.

Toluene is toxic, and the threshold limit value has been set at 200 ppm. The flammability limits in air are 1.17-7.10% by volume, and the minimum ignition temperature is 536 °C.

REFERENCES

1. *Selected Values of Properties of Hydrocarbons and Related Compounds*, American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, Texas.
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I/5

CHLOROBENZENE + ETHYLBENZENE TEST MIXTURE

Intended usage: This mixture may be used to measure the plate efficiency of columns equivalent to 7-48 theoretical plates (pressure 1013.25 mbar), 5-42 theoretical plates (pressure 400 mbar), and 3-31 theoretical plates (pressure 66.6 mbar).

Sources of supply and/or methods of preparation: Both components can be purchased and the specimens purified by distillation through a column of 50 theoretical plates using a high reflux ratio. The physical properties of the samples used to make the test mixture should be similar to the values listed under Analysis.

Analysis: Refractive index (chlorobenzene, n_D^{20} = 1.5248; ethylbenzene, n_D^{20} = 1.4959) or density (chlorobenzene, ρ^{20}/kg m^{-3} = 1106.3; ethylbenzene, ρ^{20}/kg m^{-3} = 867.02) measurements can be used to analyse mixtures.

Alternatively gas chromatography (e.g. a 2-3 m column packed with 5% by weight of Carbowax 20 M on Chromosorb G at 85 °C) or i.r. spectroscopy can be used.

Pertinent physico-chemical data: The vapour pressures of the pure components are given by the equations below. The equation for chlorobenzene is based on the data in Ref. 1, and it gives values in good accord with those in Ref. 2; the equation for ethylbenzene was taken from Ref. 3.

Chlorobenzene: $\log(p_1/\text{mbar}) = 7.11031 - 1436.135/[(t\ /°C) + 218.158]$,

Ethylbenzene: $\log(p_2/\text{mbar}) = 7.08209 - 1424.255/[(t\ /°C) + 213.206]$.

These equations yield boiling temperatures of 131.727, 100.399, 53.486 °C for chlorobenzene and 136.187, 104.706, 57.636 °C for ethylbenzene at pressures of 1013.25, 400, 66.6 mbar respectively.

Vapour-liquid equilibrium: the system is assumed to be ideal so that

$$\ln \alpha = \ln(p_1/p_1)$$

Pressure 1013.25 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0560	1.1265	27	0.5406	0.5702	1.1278
3	0.0626	0.0700	1.1265	29	0.5994	0.6280	1.1280
5	0.0781	0.0872	1.1265	31	0.6557	0.6823	1.1281
7	0.0971	0.1081	1.1266	33	0.7079	0.7322	1.1283
9	0.1201	0.1333	1.1267	35	0.7552	0.7768	1.1284
11	0.1477	0.1634	1.1267	37	0.7971	0.8159	1.1285
13	0.1803	0.1987	1.1268	39	0.8334	0.8495	1.1286
15	0.2184	0.2394	1.1269	41	0.8644	0.8779	1.1287
17	0.2619	0.2856	1.1270	43	0.8903	0.9016	1.1287
19	0.3107	0.3369	1.1272	45	0.9118	0.9211	1.1288
21	0.3641	0.3923	1.1273	47	0.9295	0.9370	1.1288
23	0.4212	0.4507	1.1275	49	0.9438	0.9499	1.1289
25	0.4806	0.5106	1.1276	50	0.9499	0.9554	1.1289

Pressure 400 mbar

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0570	1.1487	23	0.5294	0.5641	1.1505
3	0.0649	0.0739	1.1488	25	0.5982	0.6314	1.1508
5	0.0840	0.0953	1.1488	27	0.6635	0.6941	1.1510
7	0.1079	0.1220	1.1489	29	0.7232	0.7505	1.1512
9	0.1377	0.1550	1.1490	31	0.7759	0.7995	1.1514
11	0.1741	0.1950	1.1492	33	0.8211	0.8409	1.1516
13	0.2178	0.2425	1.1494	35	0.8589	0.8752	1.1517
15	0.2689	0.2972	1.1495	37	0.8898	0.9029	1.1518
17	0.3271	0.3585	1.1498	39	0.9146	0.9250	1.1519
19	0.3913	0.4250	1.1500	41	0.9343	0.9424	1.1520
21	0.4595	0.4944	1.1502	43	0.9497	0.9560	1.1520

Pressure 66.66 mbar

N+1	x	y	α	N+1	x	y	α
1	0.0500	0.0595	1.2014	19	0.5929	0.6370	1.2049
3	0.0706	0.0836	1.2015	21	0.6790	0.7183	1.2054
5	0.0988	0.1164	1.2017	23	0.7545	0.7875	1.2059
7	0.1367	0.1599	1.2019	25	0.8172	0.8436	1.2062
9	0.1862	0.2158	1.2023	27	0.8667	0.8870	1.2065
11	0.2486	0.2846	1.2027	29	0.9045	0.9195	1.2068
13	0.3237	0.3654	1.2032	31	0.9324	0.9433	1.2069
15	0.4093	0.4548	1.2037	32	0.9433	0.9526	1.2070
17	0.5010	0.5474	1.2043				

For the method for the calculation of plate equivalence from the above tables see p. 2430.

Safety: Chlorobenzene produces eye and nasal irritation at 200 ppm, at which concentration the odour is unpleasant. A threshold limit value of 50 ppm has been accepted. The flammable limits in air are 1.35-7.05% by volume and the minimum ignition temperature in air is 686 °C.

The threshold limit value for ethylbenzene is 100 ppm, the explosive limits in air are 0.99-6.70% by volume and the minimum ignition temperature in air is 432 °C.

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I/6

BENZENE + 1,2-DICHLOROETHANE TEST MIXTURE

Intended usage: This mixture may be used to measure the plate efficiencies of columns equivalent to 7-56 theoretical plates at a pressure of 1013.25 mbar.

Sources of supply and/or methods of preparation: The compounds can be obtained from many firms. A thiophen-free grade of benzene should be used. If a commercial grade of benzene which contains thiophen is purchased this impurity can be removed by repeated shaking of the sample with concentrated sulphuric acid until the acid layer stays colourless. If the material still contains paraffinic hydrocarbons as revealed by the refractive index value or by gas chromatography, they can be removed by fractional freezing of the sample. The benzene so purified should be distilled through a column before use and the physical properties of the selected fractions should be similar to those recorded under Analysis.

Commercial samples of 1,2-dichloroethane may contain other chlorinated hydrocarbons and if the sample is acidic it should be washed with water and then dried over anhydrous calcium chloride. The sample should be fractionally distilled before use and only distillate fractions with the correct physical properties (see Analysis) should be used to make the test mixture.

Analysis: Analysis by density measurement is much more accurate than analysis by refractive index although either may be used (benzene, ρ^{20}/kg m^{-3} = 879.0; n^{20}_D = 1.5011; 1,2-dichloroethane, ρ^{20}/kg m^{-3} = 1253.1; n^{20}_D = 1.4448). Ultraviolet spectroscopy has also been used for analysis.

Pertinent physicochemical data: The vapour pressures of the pure components at $t/$°C are given by the following equations (Ref. 1):

Benzene: $\log(p_1/\text{mbar}) = 7.03055 - 1211.033 /[(t/$°C$) + 220.790]$,

1,2-Dichloroethane: $\log(p_1/\text{mbar}) = 7.28356 - 1341.37 /[(t/$°C$) + 230.05]$.

These equations yield boiling temperatures of 80.100 °C for benzene and 83.512 °C for 1,2-dichloroethane at a pressure of 1013.25 mbar.

Vapour-liquid equilibrium: the system is non-ideal, indeed the (ln α)-x curve exhibits a minimum and the following equation was used to represent ln α as a power series of x. This equation was obtained by fitting an equation by least squares to the data in Ref. 2 combined with numerical data shown graphically in Fig. 2 of Ref. 3.

$$\ln \alpha = 0.15139 - 0.19157x + 0.14718x^2 \, .$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0572	1.1528	31	0.6130	0.6340	1.0934
3	0.0653	0.0743	1.1497	33	0.6544	0.6743	1.0931
5	0.0844	0.0956	1.1460	35	0.6935	0.7122	1.0934
7	0.1078	0.1212	1.1416	37	0.7302	0.7475	1.0942
9	0.1358	0.1516	1.1367	39	0.7642	0.7802	1.0952
11	0.1685	0.1864	1.1312	41	0.7955	0.8101	1.0965
13	0.2055	0.2254	1.1255	43	0.8240	0.8371	1.0980
15	0.2463	0.2679	1.1198	45	0.8495	0.8613	1.0995
17	0.2901	0.3129	1.1143	47	0.8723	0.8827	1.1011
19	0.3361	0.3596	1.1092	49	0.8923	0.9014	1.1026
21	0.3833	0.4071	1.1047	51	0.9098	0.9176	1.1040
23	0.4309	0.4546	1.1010	53	0.9248	0.9315	1.1053
25	0.4782	0.5015	1.0979	55	0.9376	0.9433	1.1065
27	0.5246	0.5473	1.0957	57	0.9485	0.9532	1.1075
29	0.5697	0.5916	1.0942				

For a method for the calculation of the plate equivalence see p. 2430.

Safety: Benzene is very toxic and the maximum concentration in air should not exceed 10 ppm. The flammable limits in air are 1.4-7.1% by volume and the minimum ignition temperature is 562°C. The odour of 1,2-dichloroethane is detectable at 100 ppm but as one can become adapted to the odour at low concentrations odour cannot be considered a reliable warning. The maximum acceptable concentration has been set at 20 ppm. In air the flammable limits are 6.20-15.90% by volume and the minimum ignition temperature is 413°C.

REFERENCES

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, Texas.
2. F. J. Zuiderweg (editor), *Recommended Test Mixtures for Distillation Columns,* European Federation of Chemical Engineering, Working Party on Distillation, Absorption and Extraction, Institution of Chemical Engineers, London (1969).
3. E. A. Coulson, J. L. Hales and E. F. G. Herington, *Trans. Faraday Soc.,* 44, 636 (1948).

I/7

2-METHYLNAPHTHALENE + 1-METHYLNAPHTHALENE TEST MIXTURE

Intended usage: This mixture is only suitable for testing columns under reduced pressure because above 133.3 mbar thermal decomposition occurs. The mixture may be used to measure the plate efficiencies of columns equivalent to 7-59 theoretical plates (pressure 133.3 mbar), 7-54 theoretical plates (pressure 66.66 mbar), 6-47 theoretical plates (pressure 13.33 mbar) and 5-41 theoretical plates (pressure 6.67 mbar).

Sources of supply and/or methods of preparation: These compounds can be purchased from various commercial sources. The compounds can be purified by distillation under reduced pressure in a column equivalent to at least 50 theoretical plates at a high reflux ratio. 2-Methylnaphthalene which has a melting temperature of 34.5_3 or 34.5_7 °C, can also be purified by recrystallization from a 1:1 methanol and water mixture. As some photodegradation has been reported the compounds should be stored in the dark.

Analysis: As these compounds are liable to some thermal degradation under the test conditions the only reliable analytical method is gas chromatography. For example a 4-m column packed with 10% Apiezon L or Silcon oil DC 550 on Chromosorb P 80-100 mesh, with hydrogen and helium as carrier gas at 180 °C with detection by thermal conductivity has been recommended. Alternatively, a 3 or 4-m column at 140 °C packed with Loc-2-R446 has been used.

Pertinent physicochemical data: The vapour pressures of the pure liquid compounds at $t/°$C are given by the following equations (Ref. 1):

2-Methylnaphthalene: $\log(p_1/\text{mbar}) = 7.19340 - 1840.268 /[(t/°C) + 198.395]$,

1-Methylnaphthalene: $\log(p_2/\text{mbar}) = 7.16082 - 1826.948 /[(t/°C) + 195.002]$.

These equations yield boiling temperatures of 164.679, 144.329, 104.851, 90.534° C for 2-methylnaphthalene and 167.776, 147.318, 107.674, 93.310 ° C for 1-methylnaphthalene at pressures of 133.3, 66.66, 13.33 and 6.67 mbar.

Vapour–liquid equilibrium: the mixture is treated as ideal so that

$\ln \alpha = \ln(p_1/p_2)$.

For each pressure the variation of ln α with composition is small and symmetrical about $x = 0.5$. It is recommended that the following values of α be used in the Fenske equation, for the pressure ranges indicated, in experiments designed so that $x + y = 1$, and in which x lies between 0.05 and 0.40 and y between 0.60 and 0.95.

Pressure/mbar	Recommended value of α	α at $x = 0.05$	α at $x = 0.95$
133.3	1.10437	1.10381	1.10493
66.66	1.11359	1.11292	1.11426
13.33	1.13868	1.13768	1.13969
6.67	1.15112	1.14994	1.15230

Safety: Little information is available on the toxicity of these compounds but every attempt should be made to prevent the escape of these materials into the atmosphere. The self ignition temperature of 1-methylnaphthalene is reported as 525 °C.

REFERENCE

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

I/8

HEPTANE + METHYLCYCLOHEXANE TEST MIXTURE

Intended usage: This mixture may be used to measure the plate efficiencies of columns equivalent to 11–82 theoretical plates at a pressure of 1013.25 mbar.

Sources of supply and/or methods of preparation: These compounds are available from a number of firms but it is essential to purchase high grade material. The heptane employed must consist solely of the normal heptane isomer and care should be taken that the sample used is suitable by establishing that it contains only one component by gas chromatographic analysis and by making measurements of density and refractive index. The results obtained should be compared with those recorded under Analysis. A suitable grade is heptane for knock-rating of engines available from Supplier (A). A sample used to make test mixtures should be fractionally distilled before use. Methylcyclohexane samples should be purified by washing with concentrated sulphuric acid, sodium carbonate solution and water. The specimen should then be dried over anhydrous calcium chloride or a molecular sieve and should be distilled until the fractions have properties approaching those of the pure compound (see Analysis).

Analysis: Mixtures can be analysed by refractive index (heptane, $n^{20}_D = 1.38764$; methylcyclohexane $n^{20}_D = 1.42312$) or density (heptane $\rho^{20}/\text{kg m}^{-3} = 683.76$; methylcyclohexane, $\rho^{20}/\text{kg m}^{-3} = 769.39$). Griswold (Ref. 2) recommended the use of refractive index as leading to smaller errors. Gas chromatography has also been used (column 4 m long, 5% by weight of Carbowax 1550 on Chromosorb G at 60 °C or 25% by weight of squalane on Chromosorb P 60-80 mesh, at 125 °C with hydrogen as carrier gas).

Whatever method of analysis is used synthetic mixtures of known composition should be analysed so that the error in the value of N resulting from analytical errors can be assessed (see Appendix for effect of errors in x and y on the value of N obtained). The importance of paying attention to the effect of errors will be realized when it is appreciated that if $y = 0.95$, one plate produces a change of only 0.00329 in the mole fraction.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/°C$ are given by the following equations:

Heptane $\qquad \log(p_1/\text{mbar}) = 7.02167 - 1264.900 /[(t/°C) + 216.544]$,

Methylcyclohexane: $\log(p_2/\text{mbar}) = 6.94790 - 1270.763 /[(t/°C) + 221.416]$.

These equations yield boiling temperatures of 98.425 °C for heptane and 100.934 for methyl-cyclohexane at a pressure of 1013.25 mbar.

Vapour liquid equilibrium: the mixture is assumed to be ideal so that

$\qquad \ln \alpha = \ln(p_1/p_2)$.

The calculated value of α at 98.425 °C is 1.07381 and at 100.934 °C is 1.07582. Therefore the recommended value of α to be used in the Fenske equation is 1.07482. This value is the antilogarithm of the mean of the logarithms of the two values of α (i.e. the geometric mean).

Safety: The threshold limit value is 500 ppm for heptane and in air the flammable limits are 1.10 - 6.70% by volume and the minimum ignition temperature is 223°C. The threshold limit value is 500 ppm for methylcyclohexane and in air the lower flammable limit is 1.15% by volume and the ignition temperature is 285 °C.

REFERENCES

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum Institute Research 44, Thermodynamic Research Center, Texas A & M University College Station, Texas.
2. J. Griswold, *Ind. Eng. Chem.,* 35, 247 (1943).

I/9

PARA-XYLENE + META-XYLENE TEST MIXTURE

Intended usage: This mixture may be used to measure the plate efficiencies of columns equivalent to 40-290 theoretical plates at a pressure of 1013.25 mbar.

Sources of supply and/or methods of preparation: Samples can be purchased from several sources. The most likely contaminants of *para-* and *meta*-xylenes are *ortho*-xylene and ethylbenzene but fortunately the presence of small amounts of these compounds will not interfere with the testing process because the methods of analysis recommended are specific for the *para-* and *meta*-isomers. Nevertheless the test mixture should be pre-distilled up the column using a high reflux ratio and only the middle fraction should be used for the tests.

Analysis: Infrared spectroscopy or gas chromatography can be used for analysis. For example, gas chromatography using a column packed with dinonylphthalate plus 5% bentone 38 on Chromosorb W can be used for analysis. A high accuracy in the analysis must be achieved if a high precision in the value for the calculated number of plates is to be obtained.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/°C$ are given by the following equations (Ref. 1):

para-Xylene: $\log(p_1/\text{mbar}) = 7.11542 - 1453.430 /[(t/°C) + 215.307]$,

meta-Xylene: $\log(p_2/\text{mbar}) = 7.13398 - 1462.266 /[(t/°C) + 215.105]$.

These equations yield boiling temperatures of 138.351 °C for *para*-xylene and 139.104 °C for *meta*-xylene for a pressure of 1013.25 mbar.

Vapour-liquid equilibrium: the mixture is assumed to be ideal so that

$\qquad \ln \alpha = \ln(p_1/p_2)$,

but as the following table shows the value of $\ln \alpha$ varies with pressure. However, as $\ln \alpha$ is to a good approximation a linear function of pressure it is recommended that a value of $\ln \alpha$ appropriate to the average pressure in the distillation column be used to calculate the number of theoretical plates by means of the Fenske equation.

p /mbar	1000	1200	1400	1600	1800	2000
ln α	0.020256	0.018945	0.017839	0.016884	0.016043	0.015292

As the value of α is near unity the importance of avoiding leakage from the still head, the importance of allowing long equilibration times and the necessity for high precision in the analysis must be particularly stressed.

Safety: The threshold limit value has been established at 100 ppm and the flammability limits in air for the *para-* and *meta*-xylenes are 1.1-7.0% by volume and 1.09-7.0% by volume and the minimum ignition temperatures are 529 °C and 528 °C respectively.

REFERENCE

1. *Selected Values of Properties of Hydrocarbons and Related Compounds,* American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas A & M University, College Station, Texas.

II/1

METHANOL + ETHANOL TEST MIXTURE

Intended usage: This mixture can be used to measure the plate efficiencies of columns of 1-11 theoretical plates (1.013 bar), 1-14 theoretical plates (3.040 bar), 1-16 theoretical plates (5.066 bar) and 1-20 theoretical plates (10.13 bar).

Sources of supply and/or methods of preparation: The compounds are available as samples of high purity from many industrial sources. The most likely impurity is water, and every time these alcohols are transferred from one container to another the water content is likely to increase unless precautions are taken. Efficient distillation of methanol can reduce the water content to 0.01%. Absolute alcohol (ethanol) contains not more than 0.07% by volume of water. The samples of both alcohols should be distilled under a high reflux ratio before use.

Analysis: Gas chromatographic methods are recommended for the analysis of these mixtures because the pure compounds are hygroscopic and are easily contaminated by water. Columns that have been recommended include 1-m lengths packed with Porapak at 100 °C and 2-m lengths packed with Chromosorb 101 at 90 °C.

Pertinent physicochemical data: The vapour pressures of the pure compounds at $t/$ C are given by the following equations (Ref. 1), which yield values over the pressure range 100-1000 kNm^{-2} in good agreement with the values presented in Ref. 2:

$$\text{Methanol:} \quad \log(p_1/\text{bar}) = 5.16233 - 1556.1 \,/[\,(t/\text{ C}) + 237.23\,] ,$$

$$\text{Ethanol:} \quad \log(p_2/\text{bar}) = 4.95959 - 1432.0 \,/[\,(t/\text{ C}) + 210.83\,] .$$

These equations yield boiling temperatures of 64.53, 95.31, 111.85 and 137.13 °C for methanol and 78.23, 109.05, 125.72 and 151.34 °C for ethanol at pressures of 1.013, 3.040, 5.066 and 10.13 bar respectively.

Vapour-liquid equilibrium: the system is not ideal; data provided by Brunner (Ref. 1), which are similar to that in Ref. 3 were used.

Pressure 1.013 bar

The following equation was used to represent ln α as a power series in x,

$$\ln \alpha = 0.48478 - 0.04343x + 0.21079x^2 .$$

N+1	x	y	α	N+1	x	y	α
1	0.0500	0.0786	1.6212	9	0.7364	0.8312	1.7632
3	0.1215	0.1830	1.6203	11	0.8992	0.9429	1.8518
5	0.2666	0.3719	1.6294	12	0.9429	0.9688	1.8800
7	0.4935	0.6198	1.6731				

Pressure 3.040 bar

The following equation was used to represent ln α as a power series in x,

$$\ln \alpha = 0.38534 + 0.03007x + 0.04706x^2 .$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0719	1.4725	9	0.5524	0.6517	1.5164
3	0.1025	0.1442	1.4754	11	0.7411	0.8153	1.5426
5	0.1994	0.2695	1.4817	13	0.8728	0.9148	1.5643
7	0.3543	0.4506	1.4947	15	0.9441	0.9638	1.5772

Pressure 5.066 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$$\ln \alpha = 0.33161 + 0.09403x - 0.04301x^2.$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0686	1.3996	11	0.6367	0.7181	1.4540
3	0.0936	0.1267	1.4050	13	0.7878	0.8443	1.4608
5	0.1697	0.2242	1.4139	15	0.8881	0.9207	1.4640
7	0.2910	0.3693	1.4267	17	0.9445	0.9614	1.4653
9	0.4564	0.5475	1.4413				

Pressure 10.13 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$$\ln \alpha = 0.25373 + 0.16961x - 0.13804x^2.$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0640	1.2994	13	0.6086	0.6786	1.3578
3	0.0818	0.1042	1.3056	15	0.7413	0.7951	1.3547
5	0.1322	0.1668	1.3149	17	0.8399	0.8761	1.3483
7	0.2092	0.2598	1.3273	19	0.9049	0.9274	1.3420
9	0.3190	0.3859	1.3415	21	0.9448	0.9581	1.3375
11	0.4586	0.5341	1.3532				

Safety: The threshold limit value for methanol is 200 ppm and in air the flammable limits are 6.72-36.50% by volume and the minimum ignition temperature is 867 °C.

The threshold limit value for ethanol is 1000 ppm and in air the flammable limits are 3.28-18.95% by volume and the minimum ignition temperature is 439 °C.

REFERENCES

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2. *Vapour pressures and critical points of pure substances,* IV: C_1 to C_{20} *Alcohols,* Item
       74023, Engineering Sciences Data Unit, London (1974).
3. F. J. Zuiderweg (editor), *Recommended Test Mixtures for Distillation Columns,* European
       Federation of Chemical Engineers, Working Party on Distillation, Absorption and Extraction
       Institution of Chemical Engineers, London (1969).

II/2

PROPENE + PROPANE TEST MIXTURE

Intended usage: This mixture is suitable for testing columns at pressures above atmospheric and at temperatures in the approximate range -4 to 62 °C. The mixture may be used to measure th plate efficiencies of columns equivalent to 3-30 theoretical plates (5.066 bar), 4-37 theoretical plates (10.13 bar), 6-44 theoretical plates (15.20 bar) and 6-56 theoretical plates (22.09 bar).

Sources of supply and/or methods of purification: Cylinders containing these compounds are available from a number of manufacturers. The individual compounds of the test mixture should be purified by distillation before use and the purities of specimens employed to make test mixtures should be established by gas chromatography (see Analysis).

Analysis: Mixtures should be analysed by gas chromatography; for example, a 1-m column packed with Duropack phenyl isocyanate/Porosil C at 25 °C has been used.

Pertinent physico-chemical data: The vapour pressures of the pure compounds at $t/°$C for the temperature ranges indicated are given by the following equations (Refs. 1-3):

Propene: $\log(p_1/\text{bar}) = 4.26975 - 945.752 /[t/°\text{C}) + 269.92]$,
for temperatures $-20 < t/°$ C < 65,

Propane: $\log(p_2/\text{bar}) = 4.31293 - 998.263 /[t/°\text{C}) + 274.35]$,
for temperatures $-10 < t/°$ C < 70.

These equations yield boiling temperatures of -4.64, 19.82, 36.36, 53.35 °C for propene and 2.31, 27.48, 44.47, 61.91 °C for propane for pressures of 5.066, 10.13, 15.20 and 22.09 bar respectively.

Vapour-liquid equilibrium: the system is not ideal, and data provided by Brunner (Ref. 1) were used.

Pressure 5.066 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$\ln \alpha = 0.2539 - 0.1128x.$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0632	1.2818	17	0.6492	0.6892	1.1980
3	0.0795	0.0994	1.2775	19	0.7256	0.7585	1.1877
5	0.1233	0.1516	1.2712	21	0.7880	0.8143	1.1794
7	0.1847	0.2224	1.2625	23	0.8375	0.8581	1.1728
9	0.2644	0.3102	1.2512	25	0.8762	0.8920	1.1677
11	0.3589	0.4093	1.2379	27	0.9059	0.9181	1.1638
13	0.4603	0.5108	1.2238	29	0.9287	0.9380	1.1608
15	0.5595	0.6059	1.2102	31	0.9460	0.9531	1.1586

Pressure 10.13 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$\ln \alpha = 0.2036 - 0.0834x.$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0604	1.2207	21	0.6576	0.6903	1.1604
3	0.0727	0.0872	1.2184	23	0.7206	0.7486	1.1543
5	0.1041	0.1237	1.2152	25	0.7742	0.7976	1.1492
7	0.1462	0.1718	1.2110	27	0.8188	0.8380	1.1449
9	0.2004	0.2320	1.2055	29	0.8554	0.8710	1.1414
11	0.2665	0.3034	1.1989	31	0.8850	0.8975	1.1386
13	0.3423	0.3828	1.1913	33	0.9088	0.9189	1.1363
15	0.4241	0.4656	1.1832	35	0.9278	0.9358	1.1345
17	0.5067	0.5469	1.1751	37	0.9430	0.9493	1.1331
19	0.5857	0.6227	1.1674	38	0.9493	0.9550	1.1325

Pressure 15.20 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$$\ln \alpha = 0.1760 - 0.0793x \ .$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0588	1.1877	25	0.6715	0.6980	1.1306
3	0.0691	0.0809	1.1859	27	0.7228	0.7460	1.1260
5	0.0944	0.1098	1.1835	29	0.7675	0.7874	1.1220
7	0.1273	0.1469	1.1805	31	0.8058	0.8227	1.1186
9	0.1687	0.1927	1.1766	33	0.8383	0.8526	1.1158
11	0.2190	0.2473	1.1719	35	0.8657	0.8777	1.1133
13	0.2776	0.3095	1.1665	37	0.8887	0.8987	1.1113
15	0.3427	0.3770	1.1605	39	0.9078	0.9162	1.1096
17	0.4119	0.4470	1.1541	41	0.9238	0.9307	1.1082
19	0.4819	0.5164	1.1477	43	0.9370	0.9428	1.1071
21	0.5500	0.5825	1.1416	45	0.9480	0.9527	1.1061
23	0.6137	0.6434	1.1358				

Pressure 22.09 bar

The following equation was used to represent $\ln \alpha$ as a power series in x,

$$\ln \alpha = 0.1435 - 0.0694x.$$

$N+1$	x	y	α	$N+1$	x	y	α
1	0.0500	0.0571	1.1503	31	0.6748	0.6957	1.1015
3	0.0651	0.0741	1.1491	33	0.7154	0.7342	1.0984
5	0.0841	0.0954	1.1476	35	0.7518	0.7685	1.0956
7	0.1078	0.1216	1.1457	37	0.7841	0.7988	1.0932
9	0.1368	0.1534	1.1434	39	0.8126	0.8255	1.0910
11	0.1715	0.1910	1.1407	41	0.8376	0.8489	1.0891
13	0.2120	0.2343	1.1375	43	0.8594	0.8692	1.0875
15	0.2579	0.2826	1.1338	45	0.8784	0.8869	1.0860
17	0.3084	0.3350	1.1299	47	0.8949	0.9023	1.0848
19	0.3623	0.3901	1.1256	49	0.9092	0.9156	1.0837
21	0.4181	0.4462	1.1213	51	0.9216	0.9272	1.0828
23	0.4741	0.5018	1.1170	53	0.9323	0.9371	1.0820
25	0.5289	0.5554	1.1127	55	0.9416	0.9458	1.0813
27	0.5812	0.6060	1.1087	57	0.9496	0.9532	1.0807
29	0.6300	0.6529	1.1049				

Safety: The threshold limit value for propane is 1000 ppm. Every effort must be made to prevent leakage of propene and propane because they are highly inflammable gases.

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APPENDIX

This appendix discusses aspects of the behaviour of fractional distillation columns and of test mixtures germane to the measurement of the theoretical plate equivalences of columns.

EFFECT OF ERRORS IN THE VALUE OF THE RELATIVE VOLATILITY RATIO

This discussion will be confined to a study of mixtures for which the relative volatility ratios are constant but the conclusions reached can be usefully extended to other test materials.

The following expression is obtained by straightforward differentiation of the Fenske equation (3) by setting $(N+1) \approx N$ and by assuming $(\alpha-1)$ is small

$$100 \, dN/N \approx -100(d\alpha)/\alpha(\alpha-1) \approx -100(d\ln \alpha)/(\alpha-1). \qquad (6)$$

Clearly the percentage error in N (*viz.* $100 \, dN/N$) depends not only on the uncertainty in α (*viz.* $d\alpha$) but also on the actual value of α so that the percentage error in N will be greater the nearer the value of α is to unity because of the term $(\alpha-1)^{-1}$. For example, suppose it were decided that the percentage error in N must be less than 5% (i.e. the error on a 100-theoretical-plate column must be less than 5 plates and that on a 20-plate column must be less than 1 plate) then the value of $100(d\alpha)/\alpha(\alpha-1)$ must be less than 5. A mixture with $\alpha = 1.05$ might be used to test a 100-plate column, so to obtain 5% accuracy in N the value of α must be known to better than 0.0025. A mixture with $\alpha = 1.25$ might be used to test a 20-plate column, so to obtain 5% accuracy in N, α must be known to better than 0.015.

Such accuracies in the values of α are not easy to achieve, especially for mixtures used for testing columns equivalent to more than 50 theoretical plates, but every attempt has been made in these recommendations to derive accurate data. It is suggested that two investigators wishing to compare the performance of fractionating equipment would be well advised to use the same data for a mixture, and it is hoped that the information in the data sheets of this report will be used in that way.

CHOICE OF THE INITIAL COMPOSITION OF THE TEST MIXTURE

If it is assumed that equal observational errors in x and y are likely to occur and that the Fenske equation (3) applies to the test mixture with α constant then it can be shown that the error in the measured plate equivalence will be least when $x+y = 1$ (i.e. when $0.5 - x = y - 0.5$ so that the liquid and vapour compositions are symmetrically arranged about a mole fraction of 0.5). There is an additional advantage in choosing this condition for making measurements because when $x+y = 1$ the effect of small deviations of the mixture from ideality on the calculated plate equivalence will often be minimized. The relation between $\ln \alpha$ and x for many slightly non-ideal mixtures can often be represented by a relation of the form of Equation (7),

$$\ln \alpha = a_0 + a_1 (1-2x), \tag{7}$$

so that the value of $\ln \alpha$ at $x = 0.5$ is a_0.

As a numerical example, consider a mixture where $a_0 = 0.1823$ and $a_1 = 0$ so that the Fenske equation yields a value of $N+1$ equal to 33 plates when $x = 0.05$ and $y = 0.95$. Now suppose the mixture had in fact been such that $a_0 = 0.1823$ and $a_1 = 0.0870$; then plate-to-plate calculations yield a value of $N+1$ equal to 36 plates when $x = 0.05$ and $y = 0.95$. Thus the value of $N+1$ differs by only 3 plates when the value of $\ln \alpha$ is constant at 0.1823 and when $\ln \alpha$ varies from 0.2693 to 0.0953 (over the range $x = 0$ to $x = 1$), a considerable change in the value of $\ln \alpha$. If conditions had been chosen so that $x+y$ did not equal unity the effect on the value of $N+1$ of this change in the value of $\ln \alpha$ would have been much greater.

To choose the best initial composition for a test mixture which is far from ideal the tables of $N+1$, x and y provided should be examined to find the composition range where the expected value of $N+1$ will produce the smallest error in the calculated number of theoretical plates.

The steps in choosing the initial composition for the boiler charge for a mixture where α is constant are as follows. Guess the plate equivalence of the column N, add 1, halve the value so found and calculate by the Fenske equation the initial composition x required to produce $y = 0.5$. This is the initial composition, x, that would be required if there were no dynamic hold-up in the apparatus. The initial composition, x_c, actually to be used can be obtained by consideration of a material balance, which leads to Equation (5),

$$x_c = x + [H_0 (0.5 - x)/B_0], \tag{5}$$

where H_0 is the volume of the hold-up and B_0 is the volume of the test mixture used. For example, if $x = 0.258$ and $(H_0/B_0) = 0.1$, then $x_c = 0.282$.

EFFECT OF EXPERIMENTAL ERRORS IN THE MOLE FRACTIONS

If the magnitudes of likely errors in x and y are assumed to be the same, and if the Fenske equation, Equation (3), is applicable with α constant, and if conditions are chosen to minimize the effect of errors in x and y (i.e. $x + y = 1$), then to find the effect of an error in the composition of the boiler contents when there is no error in the vapour composition differentiation of Equation (3) with y constant followed by division by Equation (3) and putting $y = (1-x)$ and $(N + 1) \approx N$ yields Equation (8).

$$100 \ dN/N \approx -100 \ dx \ \{2x(1-x) \ \ln[(1-x)/x]\}^{-1}. \tag{8}$$

By considerations of symmetry the effect of an error dy in y will be given by the similar expression obtained by writing y for x throughout in Equation (8). The following table gives values of

$$A = -100 \ \{2x(1-x) \ln[(1-x)/x]\}^{-1}.$$

x	$-A$	x	$-A$
0.01	1099	0.25	243
0.05	357	0.30	281
0.10	253	0.35	355
0.15	226	0.40	514
0.1760	223	0.45	1006
0.20	225		

A minimum in the value of this function occurs at $x = 0.1760$. This behaviour has not been remarked on previously by other workers, and it is here proposed that this optimum value of N should be termed N_{opt}. The value of the tabulated function does not change very rapidly in the range $x = 0.05$-0.40 but it approaches infinity as x tends to zero or to 0.50. To ensure that the errors in the values of N are not too large the range $x = 0.05$ ($y = 0.95$) provides the upper limit for the number of plates N_{max} that can be determined with a given test mixture, and the values $x = 0.40$ ($y = 0.60$) have been chosen for the lower limit for the number of plates N_{min} that can be determined with a given test mixture.

In order that the values of the function tabulated expressing $100 \ dN/N$ in terms of dx be meaningful, it is essential that the value of x should be at least $10 \ dx$. Provided this condition is satisfied the table can be used to compute the percentage error in N which will result from an estimated value of dx. For example, suppose $x = 0.05$ and $dx = 0.003$, then $100 \ dN/N$ will equal -357×0.003, i.e. -1.1%. If the standard deviation of y equals that of x and both equal 0.003 then the standard deviation in N expressed as a percentage will be

1.1 x $\sqrt{2}$ = 1.5%. Thus, the standard deviation on a 100-plate column would be 1.5 plates and on a 20-plate column 0.3 plates. If x = 0.40 (y = 0.60) then a standard deviation of 0.003 in x and y will produce a standard deviation in N expressed as a percentage of 514 x 0.003 x $\sqrt{2}$ = 2.2%. However, as less than 10 plates may be under determination in these circumstances, the error will only be of the order of 0.2 plate.

Inspection of the $N+1$, x and y values tabulated for a mixture for which α is not constant will reveal readily the error in N which will result from anticipated errors in the values of x and y.

DEPENDENCE OF THE MAXIMUM, MINIMUM AND OPTIMUM NUMBER OF THEORETICAL PLATES
THAT CAN BE MEASURED ON THE RELATIVE VOLATILITY RATIO

The values of $(N+1)_{max}$, $(N+1)_{min}$ and $(N+1)_{opt}$ have been calculated for x = 0.05, y = 0.95; x = 0.4, y = 0.6; and x = 0.176, y = 0.824 respectively, from the Fenske equation, Equation (3), treating α as a constant for a given mixture.

α	$(N+1)_{max}$	$(N+1)_{min}$	$(N+1)_{opt}$
1.005	1181	163	619
1.01	592	82	310
1.02	297	41	156
1.05	121	17	63
1.10	62	8.5	32
1.15	42	5.8	22
1.20	32	4.4	17
1.30	22	3.1	12
1.50	14	2.0	7.6
2.0	8.5	1.1	4.5
2.5	6.4	0.9	3.4

For test mixtures that show relatively large changes in the value of α in the range x = 0.05 to y = 0.95, rough values of $(N+1)_{max}$, $(N+1)_{min}$ and $(N+1)_{opt}$ may be found from the table by taking an average value of α.

VAPOUR-LIQUID EQUILIBRIUM DATA FOR TEST MIXTURES

The relative volatility ratio α for a binary mixture is defined by Equation (1), and this quantity is useful for plate-to-plate calculations because x and y are related by Equation (2). Fortunately, even for non-ideal mixtures $\ln \alpha$ can usually be expressed as a polynomial in x with only a few terms. Such a power series for $\ln \alpha$ enables $(N+1)$, x, y tables to be produced readily by a computer. Since it is just as easy to use natural logarithms for the calculations as to use logarithms to the base 10 and as natural logarithms are more convenient for thermodynamic studies they have been used widely in this report.