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PHYSICAL CHEMISTRY DIVISION

COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS AND STANDARDS  
SUBCOMMITTEE ON CALIBRATION AND  
TEST MATERIALS

RECOMMENDED REFERENCE MATERIALS  
FOR REALIZATION OF  
PHYSICOCHEMICAL PROPERTIES

Recommendations (1975)  
EDITOR: E. F. G. HERINGTON

SECTION: PRESSURE-VOLUME-TEMPERATURE  
RELATIONSHIPS

COLLATOR: D. AMBROSE

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CONTENTS

Introduction

Units

- I. Reference materials for vapour pressures at temperatures up to 770 K, critical temperatures and critical pressures
    1. Carbon dioxide
    2. Pentane
    3. Benzene
    4. Hexafluorobenzene
    5. Water
    6. Mercury
    7. Ice
    8. Naphthalene
  - II. Reference materials for vapour pressures at temperatures above 600 K
    1. Cadmium
    2. Silver
    3. Gold
  - III. Reference materials for orthobaric volumes (or densities) and critical volume (or density)
    1. Nitrogen
    2. Methane
    3. Carbon dioxide
    4. Benzene
    5. Water
  - IV. Reference materials for pressure - volume - temperature behaviour (gases)
    1. Helium (second virial coefficient)
    2. Benzene (second virial coefficient)
    3. Air
    4. Nitrogen
    5. Oxygen
    6. Methane
    7. Ethylene
  - V. Reference materials for pressure - volume - temperature behaviour (liquids)
    1. Water
- Contributors  
List of Suppliers

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## INTRODUCTION

The properties displayed on a pressure - volume - temperature ( $pVT$ ) diagram may be considered as including those of the co-existent condensed and vapour phases, (i - iii), and those of the individual phases (iv, v):

- (i) vapour pressure,
- (ii) liquid - vapour critical temperature and critical pressure,
- (iii) orthobaric volumes of liquid and vapour, including the critical volume,
- (iv)  $pVT$  properties of the unsaturated vapour or gas, and
- (v)  $pVT$  properties of the compressed liquid.

(The part of the diagram relating to a solid condensed phase is not considered here except with reference to vapour pressure.)

Recommendations are made in this section of reference materials for use in measurements involving all these properties.

### I. VAPOUR PRESSURES AT TEMPERATURES UP TO 770 K, CRITICAL TEMPERATURES AND CRITICAL PRESSURES

Measurements of vapour pressure have been reported ranging from  $10^{-10}$  Pa (Pa is defined on p.1443) up to 151 MPa (the critical pressure of mercury). The accuracy attainable varies greatly, and the present recommendations are restricted to the range of pressure from just below 0.1 Pa to 7.38 MPa (the critical pressure of carbon dioxide) and of temperature from 90 to 770 K, in which reliable and accurate methods of measurements are available, *viz.* static measurement of temperature and pressure, or ebulliometry.

Whereas ebulliometric measurements of vapour pressures near atmospheric may, if the sample is of high enough purity, be accurate within a part in  $7 \times 10^4$ , corresponding to  $\pm 0.001$  K, both above and below this range the attainable accuracy is much lower. In the range 500 kPa to the critical pressure the vapour pressures of some liquefied gases such as oxygen, methane and carbon dioxide have been measured very accurately, but there are few sets of values for compounds normally liquid, with the exception of water, that may be relied on to better than 1 part in  $10^3$  of the pressure; the vapour pressures of benzene and hexafluorobenzene are probably the best known for this class of compounds because precise and consistent measurements have been made on them in more than one laboratory. Water falls into a category of its own; there have been many investigations of its thermophysical properties, including vapour pressure, and extensive assessment of their reliability.

Below 1 kPa the attainable accuracy falls off sharply and errors of 10% in such measurements are to be expected. In general measurements of the vapour pressure of liquids can be expected to be of higher accuracy than those of solids, but ice and naphthalene are recommended as reference materials because it is doubtful whether the vapour pressure of any liquid having such a low vapour pressure as these two solids is known as accurately.

A triple point, at which solid, liquid and vapour phases are in equilibrium, being invariant is in principle particularly suitable for reference purposes, and the temperatures of several triple points are defining or secondary fixed points of the International Practical Temperature Scale of 1968. The triple-point pressure of water has been suggested as a reference pressure for low-pressure manometers, which are usually dependent upon elastic deformation of a diaphragm and require calibration (Ref. 1). However, for work of the highest accuracy the exact value of this triple-point pressure (611.2 Pa) has been in doubt (Ref. 2); it is currently under investigation (Ref. 3). Of other triple-point pressures only that of carbon dioxide (517.95 kPa) has been measured sufficiently accurately for the value to be used as a reference pressure.

The temperature range in which a vapour pressure is exerted is experimentally important, and materials with a wide range of vapour pressures and a wide range of volatilities have been included. Most of the vapour - pressure tables in these recommendations have been generated from Chebyshev polynomials fitted to the data specified. The equation used (Refs. 4, 5) is

$$(T/K) \log (p/\text{kPa}) = a_0/2 + \sum_{s=1}^n a_s E_s(x), \quad (1)$$

where  $T$  is the thermodynamic temperature (in practice,  $T_{68}$  the International Practical Kelvin Temperature),  $p$  is the pressure,  $E_s(x)$  is the Chebyshev polynomial in  $x$  of degree  $s$ , and  $x$  is a function of temperature defined as  $x = [2T - (T_{\max} + T_{\min})]/(T_{\max} - T_{\min})$ ,  $T_{\min}$  and  $T_{\max}$  being two temperatures respectively just below and just above the extreme temperatures of the measured values. The series of Chebyshev polynomials  $E_0(x) = 1$ ,  $E_1(x) = x$ ,  $E_2(x) =$

$2x^2 - 1$ ,  $E_3(x) = 4x^3 - 3x$ ,  $E_{g+1}(x) = 2xE_g(x) - E_{g-1}(x)$  may be summed by forming the coefficients  $b_n, b_{n-1}, \dots, b_s, \dots, b_0$  from  $b_s = 2xb_{s+1} - b_{s+2} + a_s$  with  $b_{n+1} = b_{n+2} = 0$ . Then

$$(T/K) \log(p/\text{kPa}) = (b_0 - b_2)/2. \quad (2)$$

An approximate solution may be obtained as

$$(T/K) \log(p/\text{kPa}) \approx (a_0 + 2xa_1)/2, \quad (3)$$

and if the value of  $T$  for a given value of  $p$  is required the approximate values of  $T$  and  $dT/dp$  obtainable from (3) allow rapid convergence of the iterative solution of (1) necessary for calculation of the exact value of  $T$ . Coefficients of the equations are given in the table below; by their use values of the pressure in kilopascals are obtained as logarithms to the base 10.

For values of vapour pressure other than those tabulated simple linear interpolation will often be adequate; more accurate values will be obtained by linear interpolation of  $\log p$  against  $1/T$ . More exact interpolation still will be obtained by fitting an Antoine equation (Ref. 6) to three of the tabulated points in the range of interest if this form is preferred to that of eqn (1).

Coefficients of eqn (1)

	$T_{\min}$	$T_{\max}$	$a_0$	$a_1$	$a_2$	$a_3$	$a_4$	$a_5$	$a_6$
	K	K							
Carbon dioxide (solid)	93	217	60.124	564.125	-3.929	0.744	0.692		
Carbon dioxide (liquid)	218	305	1779.518	291.807	0.054	0.505	0.058	0.030	
Pentane	147	470	1171.153	1093.595	-30.010	9.705	-0.092		
Benzene	285	563	2333.342	917.602	-9.000	4.577	-0.106	0.173	0.061
Hexafluorobenzene	278	517	2002.068	823.237	-10.618	4.408	-0.065	0.158	
Water	273	648	2794.0144	1430.6181	-18.2465	7.6875	-0.0328	0.2728	0.1371
			$a_7$ 0.0629	$a_8$ 0.0261	$a_9$ 0.0200	$a_{10}$ 0.0117	$a_{11}$ 0.0067		
Mercury	400	1765	8745.7706	4708.7980	13.2829	29.7025	11.7077	4.5180	
Naphthalene	230	344	301.62	791.49	-8.25	0.40			

The vapour - pressure curve terminates at the critical point, which is frequently determined by observation of the temperature of disappearance of the meniscus between liquid and vapour in a sample contained in a thick-walled sealed glass tube. Carbon dioxide, pentane, benzene and hexafluorobenzene, for which vapour pressures up to the critical temperature are given here, are all suitable as reference materials in measurements of critical temperature and pressure. Naphthalene, for which low vapour pressures only are given here but which is stable at its relatively high critical temperature, may also be used for this purpose. Water, on the other hand, otherwise attractive because of its easy availability in a pure state, is inconvenient because of its high critical pressure. Reproducibility in measurements of critical temperature  $T_c$  of  $\pm 0.05$  K or better and of critical pressure  $p_c$  of  $\pm 10^{-3} p_c$  may be looked for if the samples are sufficiently pure (purity is particularly important here as the position of the critical point is often very sensitive to amounts of impurities which would cause only a small change in the vapour pressure measured just below the critical temperature).

## II. VAPOUR PRESSURES AT TEMPERATURES ABOVE 600 K

A special group of vapour - pressure reference materials comprises the metals cadmium, silver, gold, platinum and tungsten, which will cover the temperature range 350 - 3000 K and pressure range  $10^{-7}$  - 200 Pa. The cadmium, silver and gold are supplied by the National Bureau of Standards with a certificate of purity of each sample and its vapour pressure over a range of temperature; certification of the platinum and tungsten is not yet completed. International co-operation in this project is being organized by Commission II.3 (High Temperatures and Refractories) of IUPAC. At these temperatures errors in vapour-pressure measurement may be large (up to 100% of the pressure) and use of certified reference materials will allow investigators to check whether the methods they use in this range - Knudsen, torque-Knudsen, Langmuir, and mass-spectrometric methods - are subject to systematic errors.

### III. ORTHOBARIC VOLUMES (OR DENSITIES) AND CRITICAL VOLUME (OR DENSITY)

The volumes of the saturated liquid and vapour, the orthobaric volumes, are usually related through their reciprocals, the orthobaric densities  $\rho_L$ ,  $\rho_V$ , by the well known "law of rectilinear diameters" due to Cailletet and Mathias according to which the sum of the orthobaric densities varies linearly with temperature. This may be expressed as

$$\rho_L + \rho_V = 2\rho_c + a(1 - T_r) \quad (4)$$

where  $\rho_L$ ,  $\rho_V$  are the densities of liquid and vapour,  $\rho_c$  is the critical density,  $T_r$  is the reduced temperature  $T/T_c$ , and  $a$  is a constant for each substance. In addition, the difference between the two densities may be expressed as

$$\rho_L - \rho_V = b(1 - T_r)^n \quad (5)$$

where  $b$  is a constant for each substance and  $n \approx 1/3$ . An equation of the type of (5) was proposed by Verschaffelt(7) and was applied by Goldhammer(8) and by Jüptner(9); it has since been rediscovered more than once and has been extensively discussed (Refs. 10, 11). Equation (4) allows calculation of  $\rho_c$ , and addition and subtraction of eqns (4) and (5) give  $\rho_L$  and  $\rho_V$ . However, these equations are not exact; they are empirical and extra terms must often be added for the representation of exact measurements, which are difficult in the region close to  $T_c$  - as a result, there must always be some uncertainty in the extrapolation to  $T_r = 1$  from the region where observations are made, and there is always an uncertainty of about 3% in  $\rho_c$  because of the physical indefiniteness of this property. Except when  $T_r \rightarrow 1$ ,  $\rho_V \ll \rho_L$ , and the orthobaric density of the vapour cannot be determined with the same accuracy as that of the liquid. For  $T_r$  less than about 0.8,  $\rho_V$  is very small and eqns (4) and (5) cease to be useful for the representation of the variation of  $\rho_V$  with temperature although they may still be satisfactory for  $\rho_L$ ; in these conditions  $\rho_V$  is more usually obtained by extrapolation to the vapour pressure of an equation of state representing the behaviour of the unsaturated vapour.

### IV. PRESSURE - VOLUME - TEMPERATURE BEHAVIOUR OF UNSATURATED VAPOURS OF GASES

Different reference materials or ways of expressing their properties are needed for different methods of study of the  $pVT$  properties of gases and vapours. These methods may be broadly divided into three groups:

- (i) gases and vapours at pressures up to twice atmospheric,
- (ii) gases at higher pressures over wide ranges of temperature, and
- (iii) vapours of substances liquid at room temperature, at pressures up to, usually, not more than 10 MPa.

Experiments in group (i) are usually carried out in glass apparatus, often with the prime aim of determining coefficients of the virial equation of state; whereas experiments in groups (ii) and (iii), which involve higher pressures, are carried out in metal apparatus (possibly with a glass liner). Few have been carried out at temperatures greater than 800 K. The results of these measurements are frequently presented in the first instance as isotherms either in terms of  $p$  and  $V$  or of the compression factor  $Z = pV/RT$ , and are then frequently represented by an equation of state. Equations of state and the experimental procedures have been surveyed in several reviews and books (Refs. 12 - 16).

A need additional to the standardisation of measurements arises in this section of the recommendations, *viz.* that there are occasions when, in testing large plant, large quantities of a fluid of known density must be used. The question of importance is therefore not what fluids have the best known properties, but what are the properties of the fluids that must be used because of practical considerations. Accordingly, with these needs in mind, the recommendations include the following:

- (i) Air is included in addition to nitrogen, for which more accurate data are available, because it is unlikely that nitrogen will be used on a large scale in preference to air except in the air-separation industry where nitrogen is freely available.
- (ii) Oxygen is included because operators of plant containing this gas or, more particularly, liquid, who need to conduct tests on the plant or calibrate instruments *in situ* may be reluctant to admit other fluids because of the necessity for thorough purging.
- (iii) Ethylene is included because this is an industrially important gas that is often transported by pipeline in which it is metered by volume but paid for by mass. The particular value adopted for the density of ethylene in these transactions is therefore directly convertible into money terms. Metering of ethylene with flowmeters calibrated by use of other fluids has been shown not to be sufficiently reliable for this conversion, and exact and agreed values of the density of ethylene itself are needed.

In this field, the greatest effort has been put into the study of the properties of water substance, from which have arisen the International Skeleton Steam Tables and various more detailed

tables based upon them. These are referred to in recommendation V/1 relating to water as a reference material for the pressure - volume - temperature behaviour of liquids.

A special aspect of  $pVT$  properties is that they frequently cannot be reduced to compact sets of numbers conforming to the pattern set elsewhere in these recommendations and in some instances, therefore, the recommendations here are of the best sets of tables available.

#### V. PRESSURE - VOLUME - TEMPERATURE BEHAVIOUR OF LIQUIDS

Many of the comments made above in IV also apply to this section. Whenever a liquid is required in large quantities water is the obvious choice.

#### UNITS

As far as possible SI units have been used in these recommendations, but in some instances where reference is made to other publications other units are specified. The SI unit of pressure is the newton per square metre  $N\ m^{-2}$  which has been given the name pascal, symbol Pa. The following conversion factors apply to the units likely to be used in this field:

$$1\ Pa = 10^{-5}\ bar\ exactly = 9.869\ 23 \times 10^{-6}\ atm = 7.500\ 62 \times 10^{-3}\ mmHg \\ = 1.019\ 716 \times 10^{-5}\ kgf\ cm^{-2} = 1.450\ 38 \times 10^{-4}\ lbf\ in^{-2}.$$

$$1\ atm\ (standard\ atmosphere) = 101\ 325\ Pa\ exactly \\ = 1.013\ 25\ bar\ exactly = 760.000\ mmHg \\ = 1.033\ 227\ kgf\ cm^{-2} = 14.695\ 95\ lbf\ in^{-2}.$$

$$1\ mmHg = 133.3224\ Pa = 1.315\ 79 \times 10^{-3}\ atm \\ = 1.359\ 51 \times 10^{-3}\ kgf\ cm^{-2} = 1.933\ 68 \times 10^{-2}\ lbf\ in^{-2}.$$

$$1\ kgf\ cm^{-2} = 98\ 066.5\ Pa\ exactly = 735.559\ mmHg \\ = 0.967\ 841\ atm = 14.223\ 34\ lbf\ in^{-2}.$$

$$1\ lbf\ in^{-2} = 6894.76\ Pa = 6.804\ 60 \times 10^{-2}\ atm \\ = 51.7149\ mmHg = 7.030\ 70 \times 10^{-2}\ kgf\ cm^{-2}.$$

$$1\ kg = 2.204\ 62\ lb; 1\ lb = 0.453\ 592\ 37\ kg\ exactly.$$

$$1\ in = 2.54\ cm\ exactly; 1\ cm = 0.393\ 701\ in.$$

$$1\ ft^3 = 2.831\ 68 \times 10^{-2}\ m^3; 1\ m^3 = 35.3147\ 51\ ft^3.$$

$$1\ g\ cm^{-3} = 62.4280\ lb\ ft^{-3}; 1\ lb\ ft^{-3} = 0.0160185\ g\ cm^{-3}.$$

The following provisos apply to the information on Reference Materials: (a) the recommended materials have not been checked independently by the 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) the IUPAC does not guarantee any material that has been recommended.

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I/1

Physical property: Vapour pressure

Units: kPa, K

Recommended reference material: Carbon dioxide

Range of variables: 1 - 7380 kPa, 120 - 304 K

Physical states within the range: solid and vapour, liquid and vapour

Class: Calibration and Test Material

Contributor: D. Ambrose

*Intended usage:* Carbon dioxide is recommended as a test substance for vapour-pressure measurements on relatively high-boiling gases because its vapour pressure is well established and it may easily be obtained in a state of high purity. Vapour-pressure measurements in the temperature range 120 K up to room temperature are normally made by the static method, frequently in the course of calorimetric studies, or in apparatus the design of which is based upon calorimetric practice (i.e. the thermal isolation of the equilibrium vessel by means of vacuum jackets and the elimination by careful design of unwanted flows of heat through connecting tubes) (Refs. 1 - 3). The vapour pressure of carbon dioxide at 273.15 K or 273.16 K, which is accurately known, has often been used as a standard pressure for the calibration of pressure balances and, although calibration by a standards laboratory (against a standard instrument, itself calibrated by exact measurements of the diameters of piston and cylinder) is to be preferred, measurement of the vapour pressure at 273.15 K or 273.16 K by means of a pressure balance provides a useful check upon the experimental technique. An apparatus for making this measurement by a dynamic, i.e. ebulliometric, method has been described which could be adapted for use with other gases (Ref. 4).

*Sources of supply and/or method of preparation:* At one time pure samples of carbon dioxide were prepared chemically (Ref. 5) but this is probably not now necessary. Carbon dioxide of very high purity may be bought in cylinders and the probable residual impurity is air. This may be removed by pumping in the apparatus (Ref. 6). If air is present to an appreciable extent in the cylinder, which may be checked by passing the gas into an aqueous solution of potassium hydroxide and determination of the fraction not absorbed, slow venting of a large proportion of the contents of the cylinder, i.e. a Rayleigh distillation, will reduce the residual air in the cylinder to a very low level. A more effective and less wasteful method of purification is to distil the material under reflux at 273 K (Refs. 7, 8), as is done in the apparatus mentioned above (Ref. 4).

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
Solid			
120	0.004	175	16.86
125	0.012	180	27.62
130	0.032	185	44.02
135	0.080	190	68.44
140	0.187	194.674	101.325
145	0.409	195	104.07
150	0.848	200	155.11
155	1.674	205	227.07
160	3.158	210	327.17
165	5.721	215	464.78

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
Liquid			
216.58*	517.95	265	2791
220	599.6	270	3203
225	735.6	275	3659
230	893.5	280	4160
235	1075.2	285	4711
240	1282.9	290	5317
245	1518.9	295	5982
250	1785.3	300	6713
255	2084.6	304.18†	7380
260	2419.0		

\*Triple-point temperature.

†Critical temperature.

The table has been computed from equations (p.1440) fitted to the values tabulated by Meyers and van Dusen (5), but constrained to pass through the normal sublimation temperature 194.674 K, which is a secondary reference point on the International Practical Temperature Scale of 1968 (Refs. 9, 10), and the pressure 3485 kPa at 273.15 K (Refs. 4, 6, 11). Sengers and Chen (6) have recently made accurate measurements in the range 273 K to the critical temperature that are in close agreement with the equation used here; their paper includes a comparative study of the results obtained in this range by several investigators and their summary shows that the best values of  $p$  at 273.15 K lie in the range  $(3485 \pm 0.3)$  kPa. Vukalovich and Altunin have assembled data over the full range from numerous investigations (Ref. 12). Values below 1 kPa are included above because they were included in the work on which the table is based (Ref. 5), but they are probably not of high accuracy; at higher pressures the measurements are among the most accurate that have been made and reasonable estimates of their accuracy are  $\pm 5 \times 10^{-4}p$  for  $10 \text{ kPa} < p < 518 \text{ kPa}$  and  $\pm 2 \times 10^{-4}p$  for  $p > 518 \text{ kPa}$ .

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I/2

Physical property: Vapour pressure

Units: kPa, K

Recommended reference material: Pentane

Range of variables: 7.5 - 3370 kPa, 250 - 469.7 K

Physical states within the range: liquid and vapour

Class: Calibration and Test Material

Contributor: D. Ambrose

*Intended usage:* Pentane is recommended as a test substance for use in any method of vapour - pressure measurement when liquids of comparable volatility are under investigation.

*Sources of supply and/or methods of preparation:* Pentane is normally purified by fractional distillation of suitable starting material and the process of purification may be monitored by gas chromatography. The acceptability of any sample for the present purpose may be confirmed by comparative ebulliometric measurements against water. Samples of pure pentane are available from suppliers (A), (C), (D) and (E).



*Pertinent physiochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
250	7.60	320	144.3	400	1038
260	12.98	330	145.7	410	1256
270	21.15	340	260.1	420	1507
280	33.11	350	339.4	430	1793
290	50.01	360	435.9	440	2120
300	73.170	370	551.5	450	2490
309.21	101.325	380	688.8	460	2910
310	104.07	390	850.2	469.7*	3368

\*Critical temperature.

The table has been computed from an equation (p.1440) fitted to the measurements published by Willingham, Taylor, Pignocco and Rossini (1) and by Beattie, Levine and Douslin (2); the critical temperature is that selected for API Research Project 44(3). It is desirable that values recommended for reference purposes should have been confirmed by more than one investigation; in this instance, confirmation at pressures above atmospheric is not as satisfactory as is desirable since the only other investigation (by Young (4)) of this substance in the high-pressure range, while of outstanding merit for its time, did not approach the accuracy now attainable. Pentane is recommended however because there appears to be no other liquid of comparable volatility that is more suitable; it has been preferred over diethyl ether (Ref. 5), which would otherwise have been chosen, because of its much lower solvent capacity for water and its consequent relative ease of handling without contamination by atmospheric moisture.

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I/3

Physical property: Vapour pressure

Units: kPa, K

Recommended reference material: Benzene

Range of variables: 5 - 4898 kPa, 280 - 562.1 K

Physical state within the range: liquid and vapour

Class: Calibration and Test Material

Contributor: D. Ambrose

*Intended usage:* Benzene is recommended as a test substance for any method of vapour-pressure measurement in the range 5 kPa to the critical pressure 4898 kPa. It has been used as the reference substance in the comparative ebulliometric method (Ref. 1) (see recommendation I/5 relating to the use of water as a reference substance).

*Sources of supply and/or method of preparation:* Benzene may be purified by fractional freezing of material uncontaminated by sulphur-containing compounds. This substance has been extensively used as a test material in the development of the method for testing purity by freezing point measurements; however, confirmation of the vapour pressure of a sample by comparative ebulliometric measurements against water provides an alternative way of confirming its acceptability for the present purpose. Samples of pure benzene are available from suppliers (A), (C), (D) and (E).

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
280	5.148	370	165.2	470	1366
290	8.606	380	215.9	480	1602
300	13.816	390	277.7	490	1868
310	21.389	400	352.2	500	2164
320	32.054	410	441.0	510	2494
330	46.656	420	545.5	520	2861
340	66.152	430	667.6	530	3267
350	91.609	440	808.8	540	3717
353.24	101.325	450	971.1	550	4216
360	124.192	460	1156	560	4770
				562.16*	4898

\*Critical temperature.

The table has been computed from an equation (p.1440) based upon surveys (Refs. 2, 3) of the available data. There is good agreement between values published by different workers; the normal boiling temperature should be reproducible within  $\pm 0.01$  K, and pressures above atmospheric up to the critical may be expected to be within 0.1% of the values given.

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I/4

Physical property: Vapour pressure

Units: kPa, K

Recommended reference material: Hexafluorobenzene

Range of variables: 4 - 3273 kPa, 280 - 516.7 K

Physical states within the range: liquid and vapour

Class: Calibration and Test Material

Contributor: D. Ambrose

*Intended usage:* Hexafluorobenzene may be used as a test substance for any method of vapour-pressure measurement in the range 4 kPa to the critical pressure 3273 kPa. This range is substantially the same as is covered by benzene, but hexafluorobenzene is suggested as an alternative to the latter because of the very close agreement existing between very precise investigations carried out at the Bartlesville Energy Research Center, USA (Refs. 1, 2) and at the National Physical Laboratory, UK (Refs. 3, 4).

*Sources of supply and/or methods of preparation:* Anaesthetic grade hexafluorobenzene, available from supplier (B) has proved to be of suitably high purity. The purity may be monitored by gas chromatography and confirmed by freezing point measurements; however, confirmation of the vapour pressure of a sample by comparative ebulliometric measurements against water provides an alternative way of confirming its acceptability for the present purpose.

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
280	4.314	360	124.811	450	1080
290	7.459	370	168.4	460	1298
300	12.327	380	223.0	470	1548
310	19.576	390	290.5	480	1835
320	30.007	400	372.7	490	2161
330	44.571	410	471.7	500	2533

340	64.369	420	589.5	510	2956
350	90.652	430	728.6	516.73*	3273
353.405	101.325	440	891.2		

\*Critical temperature.

The table has been computed from an equation (p.1440) based on all the sources quoted. Normal boiling temperatures should be reproducible within  $\pm 0.01$  K, and pressures above atmospheric up to the critical may be expected to be within 0.1% of the values given.

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I/5

Physical property: Vapour pressure

Units: kPa, K

Recommended reference material: Water

Range of variables: 3.66 - 22106 kPa, 273.16 - 647.31 K

Physical states within the range: liquid and vapour

Class: Calibration and Test Material

Contributors: D. Ambrose and I. J. Lawrenson

*Intended usage:* If the sample of the substance of which the vapour pressure is being measured is sufficiently pure, and temperature measurements are good to  $\pm 0.005$  K, comparative ebulliometry (i.e. the comparison of the boiling or condensation temperature of the substance with that of a reference substance, preferably water, boiling at the same pressure applied by means of a buffer gas) yields values of normal boiling points which are reproducible within  $\pm 0.01$  K, and variations in the vapour pressure of the substance at a given temperature ranging from about  $\pm 0.010$  kPa at 20 kPa to  $\pm 0.020$  kPa at 200 kPa (Refs. 1 - 4). The pressure for each observation is calculated from the known relationship between the temperature and pressure of the reference substance. For determinations of the highest accuracy corrections must be applied for the effect of the hydrostatic heads of vapour in the apparatus (Refs. 4, 5), but for more moderate accuracy (if, for example, temperatures are measured by means of mercury-in-glass thermometers) these may be ignored. Smooth boiling is essential, and special steps to ensure this are necessary at pressures below 15 kPa: water, especially, tends to bump in these conditions. Many determinations have been made in ebulliometers of the type designed by Swietoslowski(3, 6) but an improved apparatus for this application is that designed by Ambrose (1), and with this smooth boiling is obtained at pressures down to 3 kPa, the lowest at which it is practicable to operate an ebulliometer containing water. There is less difficulty in obtaining smooth boiling at pressures above atmospheric, and other apparatus has been described for use up to 500 - 800 kPa (Refs. 2, 7), and up to the critical pressure of organic compounds (Ref. 8). The ebulliometric method is well established for use at pressures up to 200 kPa, and is applicable for measurements on materials boiling, at the prevailing pressure, in the range 250 - 750 K. The ebulliometric method appears to be satisfactory at pressures above 200 kPa but it has not been widely used under such conditions, and for the most accurate measurements there may be objections in principle because of the presence of the buffer gas (Ref. 4).

Since the vapour pressure of liquid water is known more exactly than that of any other substance and adequate purification of a sample is straightforward, water is also recommended as a test material for other methods of vapour-pressure measurement provided there is no likelihood of reaction with materials of construction of the apparatus.

*Sources of supply and/or method of preparation:* Purification of water has been extensively studied (Refs. 9 - 11). For the present purpose either distilled or de-ionised water may be used; excessive fractionation should be avoided lest change in the isotopic ratio leads to measurable change in the vapour pressure.

*Pertinent physicochemical data:* Vapour pressure of water  $p$ /kPa at International Practical Kelvin Temperatures  $T_{68}$ , 273.15 K, 273.16 K, at 2 K intervals from 270 K to 646 K, and 647.31 K.

$T_{68}/K$					
273.15	0.6107				
273.16	0.6111				
	0	2	4	6	8
270	0.4842	0.5615	0.6495	0.7495	0.8630
280	0.9913	1.1361	1.2993	1.4828	1.6887
290	1.9192	2.1769	2.4644	2.7845	3.1404
300	3.5353	3.9728	4.4567	4.9909	5.5799
310	6.2281	6.9405	7.7223	8.5789	9.5161
320	10.540	11.657	12.875	14.200	15.639
330	17.202	18.896	20.730	22.714	24.856
340	27.168	29.659	32.341	35.225	38.323
350	41.648	45.212	49.029	53.113	57.478
360	62.139	67.113	72.414	78.059	84.067
370	90.453	97.237	104.44	112.07	120.17
380	128.73	137.80	147.38	157.51	168.20
390	179.48	191.37	203.89	217.08	230.96
400	245.54	260.87	276.97	293.86	311.58
410	330.15	349.61	369.98	391.30	413.60
420	436.90	461.25	486.68	513.21	540.89
430	569.75	599.82	631.15	663.76	697.71
440	733.01	769.72	807.87	847.50	888.66
450	931.37	975.69	1021.7	1069.3	1118.7
460	1169.9	1222.8	1277.7	1334.4	1393.1
470	1453.8	1516.6	1581.4	1648.4	1717.6
480	1789.0	1862.7	1938.7	2017.2	2098.0
490	2181.4	2267.3	2355.7	2446.9	2540.7
500	2637.3	2736.6	2838.9	2944.0	3052.2
510	3163.3	3277.6	3394.9	3515.5	3639.3
520	3766.5	3897.0	4031.0	4168.4	4309.4
530	4454.0	4602.3	4754.4	4910.3	5070.0
540	5233.7	5401.3	5573.1	5749.0	5929.1
550	6113.4	6302.2	6495.3	6692.9	6895.1
560	7102.0	7313.5	7529.9	7751.1	7977.3
570	8208.5	8444.8	8686.3	8933.0	9185.2
580	9442.8	9705.9	9974.6	10249	10529
590	10815	11107	11406	11710	12021
600	12338	12662	12993	13330	13674
610	14025	14383	14749	15122	15503
620	15892	16288	16693	17106	17528
630	17959	18398	18848	19307	19776
640	20256	20746	21248	21762	
647.31	22106				

The table has been computed from an equation (p.1440) based on a critical survey of all the data available (Ref. 12). The values between 273 K and 373 K are practically identical with those given in another survey restricted to that range (Ref. 13), where more detailed tables will be found. More detailed tables extending over the whole range are also available (Ref. 14). Amendment will be required in due course because the value of the triple-point pressure used here is that adopted in the internationally agreed steam tables, whereas a report of results obtained in the National Bureau of Standards indicates that the true pressure is higher ( $0.61164 \pm 0.00006$ )kPa (Ref. 15). No consequent change has been made for the present because the investigation is still in progress and it seems best to await its completion, which is expected to include measurements extending to 373 K. Amendment may also be required because of changes in the temperature scale. Definition of thermodynamic temperature by allocation of the value 273.16 K to the triple-point temperature of water has made the 'steam point' a measured instead of a defined point and investigations have indicated that the thermodynamic normal boiling point of water may be as much as 30 millikelvins below the previously defined value 373.15 K (Ref. 16). This result does not affect the expression of temperatures on IPTS-68 which will remain unchanged until amendment is agreed by the Conférence Générale des

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14. D. Ambrose and I. J. Lawrenson, *The Vapour Pressure of Water*. NPL Report Chem 24, National Physical Laboratory, Teddington (1973).
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I/6

Physical property: Vapour pressure  
 Units: kPa, K  
 Recommended reference material: Mercury  
 Range of variables: 0.1 - 800 kPa, 400 - 770 K  
 Physical states within the range: liquid and vapour  
 Class: Calibration and Test Material  
 Contributor: D. Ambrose

*Intended usage:* The range of applicability of the comparative ebulliometric method, discussed in detail in connection with the use of water as a reference substance (I/5), may be extended downwards to 0.1 kPa if mercury is used as the reference substance (Ref. 1). For accurate measurements the effect of radiation in the determination of the temperature becomes important at 500 K and upwards, and for the study of high-boiling substances (up to 750 K) there may be advantage in using mercury as the reference substance, or as a test substance for check on the apparatus. For this purpose mercury may be used at pressures up to 800 kPa.

*Sources of supply and/or method of preparation:* The mercury should be purified by established methods, which normally include treatment with nitric acid and distillation (Refs. 2, 3). It is unlikely that variation in the isotopic ratio will cause significant change in the vapour pressure, but the possibility should be considered for the most accurate measurements. Purification of mercury is discussed in greater detail in the item dealing with its use as a reference material for density measurement (Ref. 4).

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$	$T_{68}/K$	$p/kPa$
400	0.138	500	5.239	600	57.64	700	314.9
410	0.215	510	6.955	610	70.09	710	363.3
420	0.329	520	9.131	620	84.67	720	417.5
430	0.493	530	11.861	630	101.66	730	477.8
440	0.724	540	15.256	640	121.35	740	544.8
450	1.045	550	19.438	650	144.05	750	619.0
460	1.485	560	25.547	660	170.08	760	700.9
470	2.078	570	30.74	670	199.80	770	791.0
480	2.866	580	38.19	680	233.59		
490	3.899	590	47.09	690	271.83		

The normal boiling temperature of mercury 629.81 K is a secondary fixed point on the International Practical Temperature Scale of 1968 (Ref. 5). The table has been computed from the equations (p.1440) given by Ambrose and Sprake (1).

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5. *The International Practical Temperature Scale of 1968*, HMSO, London (1976).  
*Metrologia* **5**, 35 (1969); **12**, 7 (1976).

I/7

Physical property: Vapour pressure

Units: Pa, K

Recommended reference material: Ice

Range of variables: 0.1 - 611 Pa, 190 - 273.16 K

Physical states within the range: solid and vapour

Class: Calibration and Test Material

Contributor: D. Ambrose

*Intended usage:* Vapour pressures in this range of pressure are normally determined by the static method. Accurate measurement of pressure below 1000 Pa is difficult; elastic gauges are most frequently used and the validity of the results obtained by their means depends upon assumptions that are difficult to confirm. Although the vapour pressure of ice is not known with the accuracy that is desirable (Ref. 1), it is probably better known than is that of any other substance in the same range of pressure, and ice is recommended as a reference substance either for test of a method or for calibration of a pressure gauge.

*Sources of supply and/or method of preparation:* See recommendation III/5 relating to use of water as a vapour-pressure reference material.

*Pertinent physicochemical data:* Pressure  $p$  of water vapour over ice at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$
190	0.032	220	2.653	250	75.94
195	0.074	225	4.937	255	123.0
200	0.162	230	8.943	260	195.6
205	0.343	235	15.80	265	305.6
210	0.701	240	27.25	270	499.6
215	1.385	245	45.97	273.15	610.7
				273.16*	611.1

\*Triple-point temperature.

The table was computed from the equation

$$\log_{10} (p/Pa) = 12.5633 - 2670.72 (T/K)^{-1}$$

which is based on the measurements reported by Jancso, Pupezin and van Hook (2). For these measurements the assumption of linearity with pressure in the output of an elastic diaphragm gauge was made. The results are in agreement with others that have been published. The values are dependent on that adopted for the triple-point pressure, which is subject to amendment (see recommendation I/5 relating to use of water as a vapour-pressure reference material).

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I/8

Physical property: Vapour pressure

Units: Pa, K

Recommended reference material: Naphthalene

Range of variables: 0.04 - 1000 Pa, 250 - 353 K

Physical states within the range: solid and vapour

Class: Calibration and Test Material, Certified Reference Material

Contributor: D. Ambrose, I. J. Lawrenson

*Intended usage:* Naphthalene is recommended as an alternative to ice as reference material for measurements below 1000 Pa when its more convenient temperature range is an advantage. However, the vapour pressure of naphthalene is not as reliably established as is that of ice, and the pressure of water vapour over ice at its triple point is to be preferred for calibration of gauges. Naphthalene may also be used as a reference material for the determination of critical temperature and pressure.

*Source of supply and/or method of preparation:* In the past naphthalene was liable to contain thionaphthen (benzo[b]thiophen) which was difficult to remove (Ref. 1), but it is now available commercially with a low sulphur content as a chemical reagent (Ref. 2). Samples of certified purity are obtainable from suppliers (A) and (C); samples of certified vapour pressure, purified by zone-refining of micro-analytical reagent naphthalene, are available from supplier (D).

*Pertinent physicochemical data:* Pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$
250	0.036	290	4.918	330	182.9
260	0.144	300	13.43	340	389.9
270	0.514	310	34.15	350	792.0
280	1.662	320	81.39	353.43*	999.6

\*Triple-point temperature.

The table has been computed from an equation (p.1440) given by Ambrose, Lawrenson and Sprake (3); it is based on measurements made by these authors in the range 0.25 - 490 Pa (dependent, as are those for ice, on the assumption of linearity of response of an elastic diaphragm gauge) and on other values in the literature. The enthalpy of sublimation at 298 K obtained by differentiating the equation is identical with the value given in the section on enthalpy in these Recommendations (Ref. 4), and the difference between the enthalpy of sublimation at the triple point and the enthalpy of vaporization at the same temperature obtained from an equation representing the vapour pressure of liquid naphthalene is in good agreement with the result of a calorimetric measurement of the enthalpy of fusion (Ref. 4). The accuracy of the values of  $p$  in the table is assessed as  $\pm 5\%$  at  $T < 280$  K and  $\pm 2\%$  at  $T > 280$  K.

Critical temperature, 748.4 K; critical pressure, 4.051 MPa (Ref. 6).

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II/1

Physical property: Vapour pressure

Units: Pa, K

Recommended reference material: Cadmium

Range of variables:  $2.5 \times 10^{-6}$  - 15 Pa, 350 - 594 K

Physical states within the range: solid and vapour

Class: Certified Reference Material

Contributor: R. C. Paule

*Intended usage:* The vapour pressure of this certified reference sample of cadmium has been determined from a statistical analysis of measurements carried out in six laboratories where several different techniques were used-Knudsen (weight loss), torque-Knudsen and calibrated mass spectrometric methods - and the values are recommended for checking other measurements of this type (Ref. 1). The certification was carried out at the request of Commission II.3.

*Source of supply:* Certified Reference Material 746 is available from supplier (C) in the form of rods 6.35 mm diameter and 63.5 mm long; it is homogeneous and has a purity of 99.999%.

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$
350	$2.52 \times 10^{-6}$	500	$2.34 \times 10^{-1}$
400	$3.01 \times 10^{-4}$	550	2.59
450	$1.22 \times 10^{-2}$	594*	15.3

\*Melting point.

#### REFERENCE

1. R. C. Paule and J. Mandel, *National Bureau of Standards Special Publication*, 260-21. U.S. Government Printing Office, Washington D.C. (1971).

#### II/2

Physical property: Vapour pressure

Units: Pa, K

Recommended reference material: Silver

Range of variables:  $1.4 \times 10^{-7}$  - 130 Pa, 800 - 1600 K

Physical states within the range: solid and vapour, liquid and vapour

Class: Certified Reference Material

Contributor: R. C. Paule

*Intended usage:* The vapour pressure of this certified reference sample of silver has been determined from a statistical analysis of measurements carried out in nine laboratories where several different techniques were used - Knudsen, (weight loss and condensation methods), torque-Knudsen and calibrated mass spectrometric methods - and the values are recommended for checking other measurements of this type (Ref. 1). The certification was carried out at the request of Commission II.3.

*Source of supply:* Certified Reference Material 748 is available from supplier (C) in the form of rods 6.35 mm diameter and 63.5 mm long; it is homogeneous and has a purity of 99.999%.

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$
800	$1.37 \times 10^{-7}$	1235*	$3.76 \times 10^{-1}$
900	$1.50 \times 10^{-5}$	1300	1.37
1000	$6.36 \times 10^{-4}$	1400	7.90
1100	$1.35 \times 10^{-2}$	1500	35.8
1200	$1.71 \times 10^{-1}$	1600	133

\*Melting point,

#### REFERENCE

1. R. C. Paule and J. Mandel, *National Bureau of Standards Special Publication*, 260-21. U.S. Government Printing Office, Washington D.C. (1971).

#### II/3

Physical property: Vapour pressure

Units: Pa, K

Recommended reference material: Gold

Range of variables:  $1.0 \times 10^{-3}$  - 190 Pa, 1300 - 2100 K

Physical states within the range: solid and vapour, liquid and vapour

Class: Certified Reference Material

Contributor: R. C. Paule



*Intended usage:* The vapour pressure of this certified reference sample of gold has been determined from a statistical analysis of measurements carried out in eleven laboratories where several different techniques were used - Knudsen, (weight loss and condensation methods), torque-Knudsen and calibrated mass spectrometric methods - and the values are recommended for checking other measurements of this type (Ref. 1). The certification was carried out at the request of Commission II.3.

*Source of supply:* Certified Reference Material 745 is available from supplier (C) in the form of wire 1.4 mm diameter and 152 mm long; it is homogeneous and has a purity of 99.999%.

*Pertinent physicochemical data:* Vapour pressure  $p$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}/K$	$p/Pa$	$T_{68}/K$	$p/Pa$
1300	$1.01 \times 10^{-3}$	1700	1.93
1338*	$2.59 \times 10^{-3}$	1800	7.35
1400	$1.02 \times 10^{-2}$	1900	24.5
1500	$7.46 \times 10^{-2}$	2000	71.6
1600	$4.19 \times 10^{-1}$	2100	189

\*Melting point.

#### REFERENCE

1. R. C. Paule and J. Mandel, *National Bureau of Standards Special Publication*, 260-19. U.S. Government Printing Office, Washington D.C. (1970).

#### III/1

Physical property: Orthobaric volume and density

Units:  $m^3 mol^{-1}$ ,  $kg m^{-3}$

Recommended reference material: Nitrogen (relative molecular mass 28.0134)

Range of variables: 63.148 -126.2 K

Physical states within the range: saturated liquid and vapour

Class: Calibration and Test Material

Contributor: S. Angus

*Sources of supply and/or methods of preparation:* Gas of high purity is available commercially but it is probably always advisable for it to be dried before use, for example, by passage through a bed of molecular sieve.

*Pertinent physicochemical data:* Molar volume  $V_m$  and density  $\rho$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	Saturated liquid		Saturated vapour	
	$10^6 V_m$ $m^3 mol^{-1}$	$\rho$ $kg m^{-3}$	$10^6 V_m$ $m^3 mol^{-1}$	$\rho$ $kg m^{-3}$
63.148*	32.28	867.77	41 500	0.6751
70	33.32	840.77	14 760	1.898
77.348†	34.64	808.61	6 071	4.614
80	35.18	796.25	4 596	6.096
90	37.55	746.00	1 857	15.085
100	40.68	688.65	877.2	31.94
110	45.18	620.02	448.8	62.41
120	53.35	525.1	225.0	124.5
124	61.02	459.1	156.4	179.1
126.20‡	89.2	314	89.2	314

\*Triple-point temperature.

†Boiling temperature at 101.325 kPa.

‡Critical temperature.

The table is extracted from a more detailed table (Ref. 1) and is based on a critical survey and correlation of the available experimental results (Refs. 1, 2); it is consistent with the pressure - volume - temperature properties recommended for nitrogen (IV/4). Values obtained by interpolation between 124 K and the critical temperature are subject to large uncertainties.

## REFERENCES

1. R. T. Jacobsen and R. B. Stewart, *J. Phys. Chem. Ref. Data* **2**, 757 (1973).
2. R. B. Stewart and R. T. Jacobsen, *Cryogenics* **13**, 526 (1973).

## III/2

Physical property: Orthobaric volume and density

Units:  $\text{m}^3\text{mol}^{-1}$ ,  $\text{kg m}^{-3}$

Recommended reference material: Methane (relative molecular mass 16.0426)

Range of variables: 90.68 -190.555K

Physical states within the range: saturated liquid and vapour

Class: Calibration and Test Material

Contributor: S. Angus

*Sources of supply and/or methods of preparation:* Methane may be purified by chromatographic procedures (e.g. by passage through a column containing activated charcoal (Ref. 1)) or by distillation (Ref. 2). Supplies of the gas of purity 99.995% or better are available commercially.

*Pertinent physicochemical data:* Molar volume  $V_m$  and density  $\rho$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	Saturated liquid		Saturated vapour	
	$10^6 V_m$ $\text{m}^3 \text{mol}^{-1}$	$\rho$ $\text{kg m}^{-3}$	$10^6 V_m$ $\text{m}^3 \text{mol}^{-1}$	$\rho$ $\text{kg m}^{-3}$
90.68*	35.55	451.3	63 820	0.2514
100	36.55	438.9	23 690	0.6772
110	37.76	424.9	10 000	1.604
120	39.12	410.1	4 903	3.272
130	40.70	394.2	2 677	5.993
140	42.54	377.1	1 579	10.160
150	44.78	358.3	982.5	16.33
160	47.66	336.6	631.9	25.39
170	51.67	310.5	410.9	39.04
180	58.13	276.0	261.0	61.47
190	78.61	201.5	128.9	124.5
190.55†	98.9	162.2	98.9	162.2

\*Triple-point temperature.

†Critical temperature.

The table is extracted from a more detailed table (Ref. 3); it is consistent with the pressure - volume - temperature properties recommended for methane (IV/6). Values obtained by interpolation between 190 K and the critical temperature are subject to large uncertainties.

## REFERENCES

1. D. R. Douslin, R. H. Harrison, R. T. Moore and J. P. McCullough, *J. Chem. Engng Data* **9**, 358 (1964).
2. R. W. Hummel and J. A. Hearne, *Chem and Ind. Lond.* 1827 (1961).
3. S. Angus, B. Armstrong and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State: Methane*, Pergamon, Oxford (1977).

## III/3

Physical property: Orthobaric volume and density

Units:  $\text{m}^3 \text{mol}^{-1}$ ,  $\text{kg m}^{-3}$

Recommended reference material: Carbon dioxide (relative molecular mass 44.0098)

Range of variables: 216.58 - 304.21 K

Physical states within the range: saturated liquid and vapour

Class: Calibration and Test Material

Contributor: S. Angus

*Sources of supply and/or methods of preparation:* See recommendation I/1 relating to use of carbon dioxide as a vapour-pressure reference material.

*Pertinent physicochemical data:* Molar volume  $V_m$  and density  $\rho$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	Saturated liquid		Saturated vapour	
	$10^6 V_m$ $\text{m}^3 \text{mol}^{-1}$	$\rho$ $\text{kg m}^{-3}$	$10^6 V_m$ $\text{m}^3 \text{mol}^{-1}$	$\rho$ $\text{kg m}^{-3}$
216.58*	37.35	1178.4	3 134	14.04
220	37.74	1166.2	2 745	16.03
230	38.98	1129.1	1 883	23.37
240	40.40	1089.4	1 318	33.37
250	42.05	1046.6	942.0	46.72
260	44.03	999.4	682.6	64.48
270	46.50	946.4	498.0	88.37
280	49.77	884.2	361.8	121.6
290	54.64	805.4	256.2	171.7
300	64.69	680.3	164.0	268.3
304.21†	94.44	466	94.44	466

\*Triple-point temperature.

†Critical temperature.

The table is extracted from a more detailed table based on a critical survey and correlation of the available experimental results where equations suitable for use in a computer, which will reproduce these values are also given (Ref. 1). Values obtained by interpolation between 300 K and the critical temperature are subject to large uncertainties.

## REFERENCE

1. S. Angus, B. Armstrong, K. M. de Reuck, *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Pergamon, Oxford (1976).

## III/4

Physical property: Orthobaric volume and density

Units:  $\text{m}^3 \text{mol}^{-1}$ ,  $\text{kg m}^{-3}$

Recommended reference material: Benzene (relative molecular mass 78.113)

Range of variables: 290 - 562.16K.

Physical states within the range: saturated liquid and vapour

Class: Calibration and Test Material

Contributor: S. Angus

*Sources of supply and/or methods of preparation:* See recommendation I/3 relating to use of benzene as a vapour-pressure reference material.

*Pertinent physicochemical data:* Molar volume  $V_m$  and density  $\rho$  at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	Saturated liquid		Saturated vapour	
	$10^6 V_m$ $m^3 mol^{-1}$	$\rho$ $kg m^{-3}$	$10^6 V_m$ $m^3 mol^{-1}$	$\rho$ $kg m^{-3}$
290	88.54	882.3	278 710	0.2803
300	89.62	871.6	179 040	0.4363
325	92.48	844.7	68 410	1.142
350	95.60	817.1	30 760	2.539
375	99.05	788.6	15 617	5.002
400	102.94	758.8	8 686	8.993
425	107.43	727.1	5 168	15.11
450	112.8	692.7	3 368	23.19
475	119.4	654.3	2 078	37.58
500	128.1	609.7	1 356	57.60
525	141.0	554.1	874.9	89.29
550	166.1	470.4	516.7	151.2
562.16*	257	304	257	304

\*Critical temperature.

The table is extracted from a more detailed table based on a critical survey and correlation of the available experimental results (Ref. 1). Values obtained by interpolation between 555 K and the critical temperature are subject to large uncertainties.

#### REFERENCE

1. *Thermodynamic Properties of Benzene*. Report No. 73009, Engineering Sciences Data Unit, London (1973).

III/5

Physical property: Orthobaric volume and density

Units:  $m^3 mol^{-1}$ ,  $kg m^{-3}$

Recommended reference material: Water (relative molecular mass 18.0152)

Range of variables: 273.16 - 647.30K

Physical state within the range: saturated liquid and vapour

Class: Calibration and Test Material

Contributor: S. Angus

*Sources of supply and/or methods of preparation:* See recommendation I/5 relating to use of water as a vapour-pressure test material.

*Pertinent physicochemical data:* Molar volume  $V_m$  and density  $\rho$  at International Practical Kelvin Temperatures  $T_{4,8}$

$T_{4,8}$	Saturated liquid		Saturated vapour	
	$\frac{10^6 V_m}{\text{m}^3 \text{ mol}^{-1}}$	$\frac{\rho}{\text{kg m}^{-3}}$	$\frac{10^6 V_m}{\text{m}^3 \text{ mol}^{-1}}$	$\frac{\rho}{\text{kg m}^{-3}}$
273.16*	18.018	999.8	371 600	0.004 851
323.15	18.233	988.0	216 800	0.083 11
373.15†	18.799	958.3	30 140	0.597 8
423.15	19.646	917.0	7 076	2.546
473.15	20.835	864.7	2 294	7.852
523.15	22.54	799.2	903.1	19.948
573.15	25.29	712.4	390.4	46.15
623.15	31.35	574.6	158.8	113.5
633.1	34.09	528.4	125.1	144.0
643.15	39.87	451.9	88.72	203.0
647.30‡	56.84	317.0	56.84	317.0

\*Triple point temperature.

†Boiling temperature at 101.325 kPa.

‡Critical temperature.

The table is extracted from a more detailed table based on a critical survey and correlation of the available experimental results (Ref. 1); it is consistent with the pressure-volume-temperature properties recommended for water (V/l). Values obtained by interpolation between 643.15 K and the critical temperature are subject to large uncertainties.

#### REFERENCE

1. J. H. Keenan, F. G. Keyes, P. G. Hill and J.G. Moore, *Steam Tables* (International edition), Wiley, New York (1969).

#### IV/1

Physical property: Second virial coefficient

Units:  $\text{cm}^3 \text{ mol}^{-1}$

Recommended reference material: Helium (relative atomic mass 4.002 60)

Range of variables: 250 - 1500 K

Physical states within the range: gas

Class: Calibration and Test Material

Contributors: D. Ambrose, S. Angus

*Intended usage:* Measurements of  $pVT$  properties of gases or unsaturated vapours are frequently made in a Burnett apparatus, in which the ratio of two volumes must be determined either from the measurements made on the substance under study (Ref. 1) or from measurements made in a separate experiment on a gas chosen because it is nearly ideal, *viz.* hydrogen (Ref. 2), or helium (Refs. 3 - 5). The values of the second virial coefficient given here will allow calculation of the volumetric properties needed for evaluation of the volume ratio of the apparatus if helium is used for the calibration.

*Source of supply and/or method of preparation:* Helium of adequately high purity is available commercially. Purification to a higher standard for gas chromatographic use has been described (Refs. 6, 7).

*Pertinent physicochemical data:* Second virial coefficient  $B_V$  of helium at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	$B_V$ $\text{cm}^3 \text{mol}^{-1}$		$T_{68}$ K	$B_V$ $\text{cm}^3 \text{mol}^{-1}$		$T_{68}$ K	$B_V$ $\text{cm}^3 \text{mol}^{-1}$	
	±			±			±	
250	12.16	0.14	550	10.90	0.3	900	9.71	0.4
300	11.95	0.2	600	10.71	0.3	1000	9.41	0.4
350	11.73	0.2	650	10.53	0.3	1200	8.86	0.4
400	11.51	0.2	700	10.35	0.3	1300	8.60	0.4
450	11.30	0.3	750	10.18	0.3	1400	8.36	0.4
500	11.10	0.3	800	10.02	0.3	1500	8.12	0.4

The above values, calculated by McCarty (8), are those appropriate to the equation

$$pV = RT(1 + B_V/V),$$

i.e. the truncated form of the volume-explicit virial equation, which accurately represents the behaviour of helium in the temperature range given at pressures up to 10 MPa (above this pressure, a third virial coefficient  $C_V$  should be included in the equation, but values for  $C_V$  are of much lower accuracy than those for  $B_V$ ). Values of  $B_V$  are available for lower temperatures, but their accuracy is less certain, and they have been omitted because they are unlikely to be required for the purpose of this recommendation. There are other assessments of the best values for  $B_V$  (Refs. 9 - 11); those given here are the ones preferred for use in the projected IUPAC tables of thermodynamic properties. The 95% confidence levels based on a statistical analysis of the data are given in the table but the more cautious  $\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$  for the absolute accuracy of the values is recommended.

#### REFERENCES

1. E. G. Butcher and R. S. Dadson, *Proc. Roy. Soc. Lond. A* 277, 448 (1964).
2. W. H. Mueller, T. W. Leland and R. Kobayashi, *Amer. Inst. Chem. Engng J.* 7, 267 (1961).
3. L. N. Anderson, A. P. Kudchadker and P. T. Eubank, *J. Chem. Engng Data* 13, 321 (1968).
4. A. P. Kudchadker and P. T. Eubank, *J. Chem. Engng Data* 15, 7 (1970).
5. M. Waxman and J. R. Hastings, *J. Res. Nat. Bur. Std.* C75, 165 (1971).
6. P. J. Bourke, M. D. Gray and W. H. Denton, *J. Chromatog.* 19, 189 (1965).
7. C. A. Seitz, W. M. Bodine and C. L. Klingman, *J. Chromatog. Sci.* 9, 29 (1971).
8. R. D. McCarty, *Thermophysical Properties of Helium-4 from 2 to 1500 K with Pressures to 1000 Atmospheres*, National Bureau of Standards, Washington D.C. In press.
9. J. M. H. Levelt Sengers, M. Klein and J. S. Gallagher, *PVT Relations of Gases. Second Virial Coefficients*, in: *Handbook of Physics*, 3rd Edn, p. 4. McGraw-Hill, New York (1972).
10. J. Kestin and E. A. Mason, *Transport Phenomena, Conference Proceedings* 11, p. 137. American Institute of Physics (1973).
11. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases, A Critical Compilation*, Clarendon Press, Oxford (1969).

#### IV/2

Physical property: Second virial coefficient

Units:  $\text{cm}^3 \text{mol}^{-1}$

Recommended reference material: Benzene (relative molecular mass 78.1134)

Range of variables: 300 - 600 K

Physical states within the range: vapour

Class: Calibration and Test Material

Contributors: D. Ambrose, I. J. Lawrenson

Measurements in different laboratories of the second virial coefficients of substances liquid at room temperature frequently differ by more than their estimated experimental errors. Large and indeterminate errors arise, for example, when the liquid is polar and tends to be absorbed on the walls of the apparatus. The problem of adsorption is not as severe for benzene as it is for many other liquids, and benzene is one of the substances that have been studied by many investigators. A set of values of the second virial coefficient of benzene is offered here, based on an assessment (Ref. 1) of all published work (Refs. 2, 3), for use in checking apparatus for measurement of the vapour imperfections of volatile liquids.

*Sources of supply and/or methods of preparation:* See recommendation I/3 relating to use of benzene as a vapour-pressure reference material.

*Pertinent physicochemical data:* Second virial coefficient  $B_p$  of benzene at International Practical Kelvin Temperatures  $T_{68}$

$T_{68}$ K	$-B_p$ $\text{cm}^3 \text{mol}^{-1}$	$T_{68}$ K	$-B_p$ $\text{cm}^3 \text{mol}^{-1}$	$T_{68}$ K	$-B_p$ $\text{cm}^3 \text{mol}^{-1}$
300	1452	420	631	520	397
320	1222	440	569	540	367
340	1045	460	516	560	341
360	907	480	471	580	317
380	796	500	431	600	296
400	706				

These values have been calculated from the equation (Ref. 1),

$$B_p / \text{cm}^3 \text{mol}^{-1} = 201.925 - 150.07 \exp 720 (T_{68}/\text{K})^{-1},$$

which represents the 72 selected data points extending over the range of the table with a r.m.s. deviation of 2%, maximum deviations (observed values minus calculated) -3%, +5%.

The second virial coefficient given is that appropriate to the equation,

$$V = RT/p + B_p,$$

i.e. the truncated form of the pressure-explicit virial equation (Ref. 4).

#### REFERENCES

1. D. Ambrose and I. J. Lawrenson, *Proc. Tech. Int.* 17, 968 (1972).
2. J. H. Dymond and E. B. Smith, *The Virial Coefficients of Gases. A Critical Compilation.* Clarendon Press, Oxford (1969).
3. P. G. Francis, M. L. McGlashan and C. J. Wormald, *J. Chem. Thermodynamics* 1, 441 (1969).
4. J. D. Cox and I. J. Lawrenson, *Specialist Periodical Report: Chemical Thermodynamics* (senior reporter M. L. McGlashan), Vol. 1, p. 162. The Chemical Society, London (1972).

#### IV/3

Physical property: Pressure - volume - temperature relationships

Units: bar,  $\text{cm}^3 \text{g}^{-1}$ , K

Recommended reference material: Air (effective relative molecular mass 28.966)

Range of variables: 150 - 1000 K, 1 - 1000 bar

Physical states within the range: gas

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* For tests requiring large quantities of gas, air is the obvious choice except at cryogenic temperatures.

*Sources of supply and/or methods of preparation:* For accurate measurements the air should be freed from carbon dioxide and water by, for example, passage through beds of suitable adsorbant. Removal of trace contaminants from laboratory air is discussed by Williams and Eaton (1), but such ultra-purification should not be necessary for the present purpose.

*Pertinent physicochemical data:* Use of the tables by Sytchev, Kozlov and Spiridonov (2) is recommended. These tables give values of the specific volume and its derivatives, enthalpy, entropy, heat capacities, Joule - Thomson coefficient and fugacity in pressure-temperature co-ordinates. The equation of state is given. The tables are based on a critical survey and correlation of the available experimental data up to about 873 K, 700 bar; values at higher temperatures and pressures were obtained by extrapolation. Reference 2, which is in Russian, is not easily accessible and until an English translation is available, which it is hoped will have a wider circulation, the tables by Baehr and Schmier(3) may be used. These give values of specific volume, enthalpy, entropy and exergy from 63 to 1077 K (in °C) up to 4500 bar. (*Exergy* is the excess Gibbs energy over that under ambient conditions defined as 1 bar, 15 °C). The tables were prepared before the high-temperature high-pressure results were available,

and consequently they have a larger region depending upon extrapolation than those in Ref. 1. Below 473 K the two sets of tables do not differ significantly.

## REFERENCES

1. F. W. Williams and H. G. Eaton, *Analyt. Chem.* **46**, 179 (1974).
2. V. V. Sytchev, A. D. Kozlov and G. A. Spiridonov, *Teplofizicheskie Svoistva Veshchestv i Materialov* **5**, 4 (1972).
3. H. D. Baehr and K. Schwier, *Die thermodynamischen Eigenschaften der Luft*, Springer-Verlag OHG, Berlin (1961).

## IV/4

Physical property: Pressure - volume - temperature relationships

Units: bar, mol l<sup>-1</sup>, K

Recommended reference material: Nitrogen (relative molecular mass 28.0134)

Range of variables: Melting line (ca. 64 - 66 K) - 2000 K, 0.1 - 100 bar;  
Melting line (ca. 66 - 195 K) - 1200 K, 120 - 10 000 bar

Physical states within the range: liquid and gas

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* For tests requiring large quantities of inert gas or liquid, nitrogen is the most readily available substance.

*Sources of supply and/or methods of preparation:* Gas of high purity is available commercially, but it is probably always advisable for it to be dried before use, for example by passage through a bed of molecular sieve.

*Pertinent physicochemical data:* Use of the tables by Jacobsen and Stewart (1) is recommended. These tables give values of the density and its derivatives and of the internal energy, enthalpy, entropy, heat capacities and speed of sound in pressure - temperature co-ordinates. The equation of state is given, together with its subsidiary forms necessary to calculate the above properties. The tables are based on a critical survey and correlation of the available data.

## REFERENCE

1. R. T. Jacobsen and R. B. Stewart, *J. Phys. Chem. Ref. Data* **2**, 757 (1973).

## IV/5

Physical property: Pressure - volume - temperature relationships

Units: atm, cm<sup>3</sup> mol<sup>-1</sup>, K

Recommended reference material: Oxygen (relative molecular mass 31.998)

Range of variables: 54.351 K, 0.001 atm (triple point) to 340 K, 340 atm

Physical states within the range: liquid and gas

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* When equipment is used with liquid oxygen, or when equipment is used in which a phase change may occur as a result of which oxygen liquefies, it may be necessary on grounds of safety for *in situ* calibrations and tests to be carried out only with oxygen.

*Sources of supply and/or methods of preparation:* Oxygen of high enough purity for most purposes may be bought. A more detailed consideration of the purity of the gas will be found in work relating to the use of its normal boiling point as a defining temperature of the International Practical Temperature Scale (Refs. 1 - 3).

*Pertinent physicochemical data:* Use of the tables by Roder and Weber is recommended (4). These give values of density, internal energy, enthalpy, entropy and several of their derivatives, the velocity of sound, dielectric constant, thermal conductivity, viscosity, thermal diffusivity and Prandtl number. In addition, many of the properties are shown graphically and there is a critical survey of the data with a comprehensive bibliography.



## REFERENCES

1. J. Ancsin, *Metrologia* **6**, 53 (1970).
2. J. Ancsin, *Temperature*, Vol. 4, Part 1 (Editor-in-Chief, H. H. Plumb), p. 211. Instrument Society of America, Pittsburgh (1972).
3. J. L. Tiggelman and M. Durieux, *Temperature*, Vol. 4, Part 1 (Editor-in-Chief, H. H. Plumb), p. 149. Instrument Society of America, Pittsburgh (1972).
4. H. M. Roder and L. A. Weber, *Aerospace Safety Research and Data Institute Oxygen Technology Survey*, Vol. I. Scientific and Technical Information Office, National Aeronautics and Space Administration, Washington D.C. (1972).

## IV/6

Physical property: Pressure - volume - temperature relationships

Units: bar,  $\text{dm}^3 \text{mol}^{-1}$ , K

Recommended reference material: Methane (relative molecular mass 16.0426)

Range of variables: 90.68 K, 0.117 bar (triple point) to 500 K, 700 bar

Physical states within the range: liquid and gas

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* Testing of gas compressibility apparatus of various types - constant volume, variable volume, and expansion (Refs. 1 - 3).

*Sources of supply and/or methods of preparation:* See recommendation III/2 relating to use of methane as an orthobaric-critical volume reference material.

*Pertinent physicochemical data:* The tables prepared by the IUPAC Thermodynamic Tables Project are recommended (Ref. 4). They are based on a critical review of the available experimental results and extend from the triple point to 10 000 bar, 470 K and to 400 bar from 470 K to 620 K. The tables give values of volume, entropy, enthalpy, isobaric heat capacity, compression factor, fugacity/pressure ratio, Joule - Thomson coefficient, the ratio of the heat capacities and the speed of sound as functions of pressure and temperature; and the pressure, entropy, internal energy and isochoric heat capacity as functions of density and temperature. Subsidiary tables give the zero-pressure properties, saturation-curve properties, and melting-curve properties. Equations to reproduce the tables are also given.

## REFERENCES

1. R. T. Ellington and B. E. Eakin, *Chem. Engng Prog.* **59** (11), 80 (1963).
2. E. A. Mason and T. H. Spurling, *The Virial Equation of State*, Pergamon, Oxford (1969).
3. J. D. Cox and I. J. Lawrenson, *Specialist Periodical Report: Chemical Thermodynamics* (senior reporter M. L. McGlashan), Vol. 1, p. 162. The Chemical Society, London (1973).
4. S. Angus, B. Armstrong and K. M. de Reuck, *International Thermodynamic Tables of the Fluid State: Methane*, Pergamon, Oxford (1977).

## IV/7

Physical property: Pressure - volume - temperature relationships

Units: bar,  $\text{cm}^3 \text{mol}^{-1}$ , °C

Recommended reference material: Ethylene (relative molecular mass 28.1536)

Range of variables: 223.15 - 423.15 K up to 3000 bar and 223.15 - 423.15 K up to  $0.0225 \text{mol cm}^{-3}$

Physical states within the range: liquid and gas

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* Flowmeters in use in ethylene pipelines, the standards against which they are calibrated, and proposed mass-flowmeters for ethylene, require such accuracy that calibration with other fluids is not satisfactory, and the properties of ethylene itself are required. In the region of the critical point, however, these properties are not themselves sufficiently accurately known to meet the practical needs; work is in progress with the aim of improving the data in this region.

*Sources of supply and/or methods of preparation:* Ethylene of high purity may be bought; commercial grades may contain other hydrocarbons that will change its properties, especially near the critical point. Calculations based on analysis should be made to check the possible effects before the values in the tables are applied.

*Pertinent physicochemical data:* The tables prepared by the IUPAC Thermodynamic Tables Project Centre (Ref. 1) are recommended. These tables give values of density, internal energy, enthalpy, entropy, heat capacities, fugacity and speed of sound in pressure - temperature coordinates and in density - temperature coordinates, and are based on a critical survey of the available experimental data without any extrapolation. The equations by which the tables were generated are given but the user is recommended to obtain values needed by interpolation in the tables. Another set of tables (Ref. 2) gives values of density only at very small intervals of temperature and pressure in the range - 30 to 75°C up to 100 bar. These tables agree with those of Ref. 1 within 0.1% of the density, except near the critical point and at their highest pressures where use of Ref. 1 is to be preferred. The units are bar, kg m<sup>-3</sup>, °C and the tables are available alternatively with the pressure in atmospheres.

## REFERENCES

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2. W. Thomas, M. Zander, G. Quietzsch and H. Schuchmann, *Dichte des Äthylens im Emphasengebiet für Temperaturen von - 30 °C bis 75 °C bei Drücken bis 100 bar*. Fabwerke Hoechst AG, Frankfurt (M) - Hoechst (1972).

V/1

Physical property: Pressure - volume - temperature relationships

Units: bar, cm<sup>3</sup> g<sup>-1</sup>, °C

Recommended reference material: Water (relative molecular mass 18.0152)

Range of variables: 273.16 K, 0.001 bar (triple point) to 653 K, 1400 bar

Physical states within the range: liquid

Class: Calibration and Test Material

Contributor: S. Angus

*Intended usage:* For tests and calibrations requiring large quantities of liquid with well defined physical properties, water is the obvious choice for all pressures at ambient or near-ambient temperatures. The volumetric properties of water are better known than are those of any other liquid but it is corrosive and attacks both glass and silica (although the latter more slowly) at elevated temperatures; this is of importance in relation to its use as a reference material for density.

*Sources of supply and/or methods of preparation:* See item I/5 relating to use of water as a vapour-pressure material.

*Pertinent physicochemical data:* There exist several tables (Refs. 1 - 6) based on the 1963 International Skeleton Table (IST 1963), which itself is based on the experimental data available up to 1960, but it is recommended that the values used for liquid water be those given in the tables by Keenan, Keyes, Hill and Moore (7) (the reference is to the edition in metric units; there is another edition in English units). These tables are based on a re-analysis of the data including what became available between 1960 and 1966, and they differ from IST 1963 where there is compelling reason for change. Table 4 of Ref. 7 gives density, internal energy, enthalpy and entropy of water from 0 °C to 380 °C up to 1400 bar. Other tables give the properties of steam, properties in the critical region, viscosity and thermal conductivity. The equation from which the tables were generated is given. If values are required at higher pressures, 1000 - 100 000 bar, the work by Jůza may be consulted (Ref. 8). In all the tables the International Practical Temperature Scale of 1948 is used.

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8. J. Jůza, *An Equation of State for Water and Steam*, Academia, Prague (1966).

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