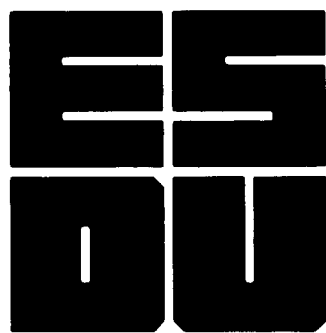




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Normal melting points, boiling points and critical points of n-alkyl aldehydes and ketones

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ENGINEERING SCIENCES DATA ITEM NO.71023

Chemical Engineering Series

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NORMAL MELTING POINTS, BOILING POINTS AND CRITICAL POINTS OF n-ALKYL ALDEHYDES AND KETONES

1. INTRODUCTION

The liquids for which data are presented in this Item are the normal (i.e. straight chain) alkanals (alkyl aldehydes) and alkanones (alkyl alkyl ketones) and are listed below:

- | | | |
|-----|--|-------------|
| (a) | $\left\{ \begin{array}{ll} \text{alkanals} & (\text{alkyl aldehydes})C_1-C_5 \\ \text{alkanals} & (\text{alkyl aldehydes})C_6-C_{20} \end{array} \right\}$ | Table I, |
| (b) | <u>alkan-2-ones</u> (methyl alkyl ketones) | Table II, |
| (c) | <u>alkan-3-ones</u> (ethyl alkyl ketones) | Table III, |
| (d) | <u>alkan-4-ones</u> (propyl alkyl ketones) | Table IV, |
| (e) | <u>alkan-5-ones</u> (butyl alkyl ketones) | Table V, |
| (f) | <u>alkan-6-ones</u> (pentyl alkyl ketones) | Table VI, |
| (g) | <u>alkan-7-ones</u> (hexyl alkyl ketones) | Table VII, |
| (h) | <u>alkan-8-ones</u> (heptyl alkyl ketones) | Table VIII, |
| (i) | <u>alkan-9-ones</u> (octyl alkyl ketones) | Table IX, |
| (j) | <u>alkan-10-ones</u> (nonyl alkyl ketones) | Table X. |

The names underlined above and given in the first column of the Tables are those recommended by the BSI in Reference 1. The other names are in general the most widely used of other synonyms.

The Tables also give the molecular weights and the empirical and structural formulae. The molecular weights have been calculated from the atomic weights given in Item No.68043.

Experimental values of normal melting and normal boiling points are available for less than half the compounds considered and only a few determinations of the critical temperatures and critical pressures have been made. The method of correlating these data and estimating the values given in the Tables is outlined in Section 4. Values in italics denote that no experimental data were available. It should be noted that for some compounds the normal boiling point and/or critical temperature so derived may be above the decomposition temperature. However, hypothetical values at these temperatures are sometimes necessary for calculating the properties of solutions.

Section 5 refers to three recommended methods which may be used to estimate boiling points at any particular pressure and which require data from this Item only.

2. NOTATION

P_{br}	reduced pressure of normal boiling point, i.e. $1/P'_c$	
P_c	critical pressure	10^5 N/m^2
P'_c	critical pressure, $(0.9869 P_c)$	atm.
T	temperature	K
T_b	normal boiling point, $(t_b + 273.15)$	K
T_{br}	reduced temperature of normal boiling point, i.e. $\frac{T_b}{T_c}$	
T_c	critical temperature, $(t_c + 273.15)$	K
t	temperature	$^{\circ}\text{C}$
t_b	normal boiling point	$^{\circ}\text{C}$
t_c	critical temperature	$^{\circ}\text{C}$

3. CONVERSION FACTORS

$$\text{Temperature in degrees Fahrenheit} = \frac{9}{5}t + 32$$

$$\text{Temperature in degrees Rankine} = \frac{9}{5}T$$

$$\begin{aligned}
 10^5 \text{ N/m}^2 &= 1 \quad \text{bar} \\
 &= 14.5038 \text{ lbf/in}^2 \\
 &= 1.0197 \text{ kgf/cm}^2 \\
 &= 0.9869 \text{ Standard Atmosphere} \\
 &= 750.062 \text{ mmHg.}
 \end{aligned}$$

4. DERIVATION OF NORMAL MELTING POINTS, NORMAL BOILING POINTS AND CRITICAL POINTS

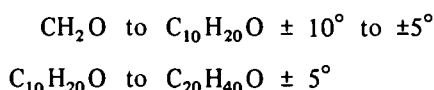
The normal melting point and normal boiling point data that are available for the compounds considered have been taken from Derivation 6, and the available critical temperature and critical pressure data from Derivation 5. The melting and boiling point data for compounds with carbon numbers up to seven (C_7) are critically evaluated in Derivation 3 which also gives melting points and extrapolated values of normal boiling point up to high carbon numbers for alkanals and alkan-2-ones. Accurately determined values of melting points for a number of ketones are given in Derivations 4 and 7. Using the data of Derivation 3 up to C_7 as a basis, values of the normal melting points and normal boiling points of all the straight chain alkanals and alkanones up to C_{20} have been determined by the method outlined below. For the alkanals and alkan-2-ones, this method gives progressively higher values of normal boiling point than Derivation 3 as C_n is increased.

Each compound is a member of two identical homologous series: one series in which the first alkyl radical is the same (i.e. methyl alkyl ketones, ethyl alkyl ketones, etc.) and another series in which the second alkyl radical is the same (i.e. alkyl methyl ketones, alkyl ethyl ketones, etc.). For each of the above four physical properties the experimental data may be plotted in carpet form so that the value for each compound may be assessed in each of its relevant series. In smoothing and extrapolating these data to derive the values given in the Tables the following assumptions have been made.

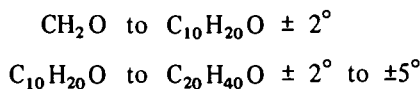
- (a) For each series, the variation of each physical property with carbon number is a smooth function as is the case for the parent alkanes.
- (b) For an infinite chain length the compounds and their parent alkanes have the same normal melting point, the same normal boiling point and the same critical point since the structural differences between the compounds and their parent alkanes become negligible as the chain length tends to infinity.
- (c) Between isomers there is a smooth variation of each physical property considered.

The above procedure enables a self consistent set of data to be obtained for the complete range of compounds considered although the overall accuracy may be expected to vary. The user should therefore allow for some uncertainty in values of the temperatures and critical pressures given in the Tables as detailed below:—

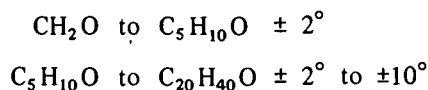
- (a) normal melting points*,



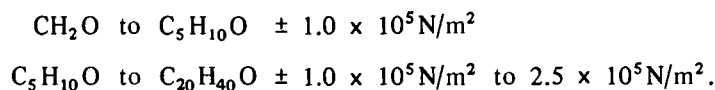
- (b) normal boiling points,



- (c) critical temperatures,



- (d) critical pressures,



* In the literature widely varying values of melting points are reported for some substances. Certainly some compounds may appear to melt over a range of temperature rather than at a single temperature due to various phenomena, e.g. the existence of more than one crystalline form. Moreover, some substances require an excessive time to reach thermodynamic equilibrium and this may account for other anomalous values. The compounds considered here are reasonably certain to be liquid above the temperatures quoted as melting points.