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International Journal of Thermal Sciences 44 (2005) 197–209
International Journal of Thermal Sciences
www.elsevier.com/locate/ijts

Psychrometric charts for organic vapours 1. Ketones in air

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Received 9 February 2004; accepted 30 March 2004

Abstract

Psychrometric charts for five different condensing ketone vapours in air at 100 kPa are pressures are presented. The charts are based upon semi-theoretical equations and make use of published physical property data and correlations. The behaviour of the vapour phase is characterised by the virial equation of state truncated at the third term. The solubility of gas in the liquid ketones is also considered. The charts are constructed with the dry bulb temperature and absolute humidity scales as the orthogonal axes. Curves of constant adiabatic saturation temperature, constant relative humidity, constant gas specific volume and constant enthalpy deviation are plotted on the charts.

Keywords: Psychrometric charts; Ketones; Virial equation; Humidity; Acetone

1. Introduction

Psychrometric charts are a way in which physical property data may be presented diagrammatically for systems in which one component of a gaseous mixture may condense. While accurate charts are readily available for the conventional water–air system, only recently have charts been prepared for other important systems [1]. Ketones are an important class of chemical finding application as solvents and widely used as starting and intermediate ingredients in the production of a range of materials including resins, plastics and lacquers. As the vapour pressures of these ketones can be relatively high even at ambient temperatures significant levels of ketone vapours can exist in air when they are being used. For example, even at just 21 °C as much as 0.70 kg of propanone (the commerically-important solvent acetone) vapour can exist per 1 kg of dry air.

The author described the theory behind the construction of psychrometric charts [1–3]. In this paper this method will be applied to construct a series of psychrometric charts for five ketone vapours in air. The five ketones are propanone, 2-butanone, 3-methyl-2-butanone, 3-pentanone and 2-hexanone. All charts are prepared for a total system pressure of 100 kPa.

2. Gas phase behaviour and saturation

At even relatively low pressures the gas mixture of ketone vapour and air will not behave ideally. From the many different methods by which the non-ideal behaviour of gas may be characterized, the virial equation of state is used. This method is chosen because it is relatively simple to apply and because considerable data is available for the required parameters for each of the systems studied. The virial equation of state truncated at the third term is:

$$\frac{P_T \widehat{V}}{RT} = 1 + \frac{B_m}{\widehat{V}} + \frac{C_m}{\widehat{V}^2} \tag{1}$$

where, P_T is the total pressure, $\widehat{V}$ is the molar volume of the gas mixture, R is the gas constant, T is the absolute temperature, and B_m and C_m are the second and third virial coefficients of the gas, respectively.

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doi:10.1016/j.ijthermalsci.2004.03.009

Nomenclature

B	second virial coefficient
c	correlation coefficient
C	third virial coefficient
C_P	ideal gas heat capacity
f	enhancement factor
g_1, g_2	functions defined in Eqs. (A.14) and (A.15)
$\hat{h}$	real gas specific enthalpy
$\hat{h}_{\text{dev}}$	enthalpy deviation
$\hat{h}_f$	condensed phase enthalpy
$\hat{h}'_0$	enthalpy correction
k_H	Henry's law constant
MW	molecular weight
P_C	critical pressure
P_V	vapour pressure
P_T	total pressure
R	Universal gas constant
T	absolute temperature
T_{ad}	adiabatic saturation temperature
T_C	critical temperature
T_{datum}	enthalpy datum temperature
T_r	reduced temperature
$\widehat{V}_C$	critical volume
$\widehat{V}_{V_c}$	liquid molar volume
x	mole fraction
Z_C	critical compressibility factor

Greek letters

ϕ	relative humidity
κ	isothermal compressibility
λ	latent heat of vaporization
ω	acentric factor

Subscripts

G	non-condensing gas component, i.e., air
m	mixture
S	saturation condition
V	condensing vapour component, i.e., ketone vapour

In the development of the equations which follows we shall assume that there are only two components in our system. The vapour component that readily condenses (i.e., the ketone) will be denoted V, and the gas component (i.e., the air) will be denoted G.

If x_G is the mole fraction of the non-condensing component (in this case nitrogen) and x_V is the mole fraction of the condensing component (i.e., the alcohol) then for a binary system it may be shown that:

$$B_m = x_G^2 B_{GG} + 2x_G x_V B_{GV} + x_V^2 B_{VV} \tag{2}$$

$$\begin{aligned} C_m = {} & x_G^3 C_{GGG} + 3x_G^2 x_V C_{GGV} \\ & + 3x_G x_V^2 C_{GVV} + x_V^3 C_{VVV} \end{aligned} \tag{3}$$

Here B_{ii} is the second virial coefficient of pure component i, B_{GV} is the second virial interaction (or cross) coefficient for the binary system, C_{iii} is the third virial coefficient of pure component i, and, C_{GGV} and C_{GVV} are the third virial interaction parameters. The virial coefficients are all functions of temperature alone, and are either known or may be estimated for most binary systems.

A gas is saturated with a vapour when the partial pressure of the vapour is equal to its vapour pressure at the particular temperature. For an ideal system we could write an expression relating the mole fraction of the condensing vapour component at saturation, V, to its vapour pressure:

$$x_{V_s} = \frac{P_V}{P_T} \tag{4}$$

and

$$x_{G_s} = \frac{P_T - P_V}{P_T} \tag{5}$$

where, x_{V_s} and x_{G_s} are the mole fractions of components V and G respectively at saturation, and P_V is the vapour pressure of component V. However, since the system is not ideal Hyland and Wexler [4] proposed the use of an enhancement factor. Eq. (4) becomes,

$$x_{V_s} = \frac{f P_V}{P_T} \tag{6}$$

A similar expression may be written for the non-condensing gas component G:

$$x_{G_s} = \frac{P_T - f P_V}{P_T} \tag{7}$$

The enhancement factor accounts for the effects of the dissolved gases and pressure on the properties of the condensed phase, and the effect of intermolecular forces on the properties of the moisture itself. Typically the value for the enhance factor does not exceed 1.05 for any given system [1]. The enhancement factor may be written in terms of the virial coefficients and other properties of the system [4]:

$$\begin{aligned} \ln f = {} & \left[\frac{(1+\kappa P_V)(P_T - P_V) - \frac{1}{2}\kappa(P_T^2 - P_V^2)}{RT}\right]\widehat{V}_{V_c} \\ & + \ln(1 - k_H x_{G_s} P_T) + \frac{x_{G_s}^2 P_T}{RT} B_{GG} - \frac{2x_{G_s}^2 P_T}{RT} B_{GV} \\ & - \left[\frac{P_T - P_V - x_{G_s}^2 P_T}{RT}\right] B_{GG} \\ & - \frac{2x_{G_s}^3 (2 - 3x_{G_s}) P_T^2}{(RT)^2} B_{GG} B_{GV} \\ & - \frac{x_{G_s}^2 (1 - 3x_{G_s})(1 - x_{G_s}) P_T^2}{(RT)^2} B_{GG} B_{VV} \end{aligned}$$

$$
\begin{aligned}
&+\frac{6x_{G_s}^2(1-x_{G_s})^2P_T^2}{(RT)^2}B_{VV}B_{GV}\\
&-\frac{2x_{G_s}^2(1-x_{G_s})(1-3x_{G_s})P_T^2}{(RT)^2}B_{GV}^2\\
&-\left[\frac{P_V^2-(1+3x_{G_s})(1-x_{G_s})^3P_T^2}{2(RT)^2}\right]B_{VV}^2\\
&-\frac{3x_{G_s}^4P_T^2}{2(RT)^2}B_{GG}^2+\frac{3x_{G_s}^2(1+2x_{G_s})P_T^2}{2(RT)^2}C_{GGV}\\
&-\frac{3x_{G_s}^2(1-x_{G_s})P_T^2}{(RT)^2}C_{GVV}\\
&-\left[\frac{(1+2x_{G_s})(1-x_{G_s})^2P_T^2-P_V^2}{2(RT)^2}\right]C_{VVV}\\
&+\frac{x_{G_s}^3P_T^2}{(RT)^2}C_{GGG}
\end{aligned}
\qquad (8)
$$

Here κ is the isothermal compressibility of the condensing component (i.e., the hydrocarbon), $\widehat{V}_{V_c}$ is the molar volume of the condensed component V (either as a liquid or a solid), and k_H is the Henry's law constant to account for the solubility of component G in the condensed phase. For a given temperature and total pressure, P_T, Eqs. (7) and (8) may be solved iteratively for the enhancement factor, f, and the mole fraction of component G at saturation, x_{G_s}. In practice this is done by first setting $f = 1$. x_{G_s} is then calculated using Eq. (7) and then this value is used in Eq. (8) to calculate an estimate for the enhancement factor, f. The value for x_{G_s} is then re-calculated. The cycle is then repeated until the values for f and x_{G_s} no longer change significantly between successive calculations.

The absolute humidity at saturation, H_s, is the mass of the vapour component V per mass of component G. It may be expressed in terms of the mole fractions of the two components in the gas phase at saturation:

$$H_s = \frac{x_{V_s}}{x_{G_s}}\frac{MW_V}{MW_G} \qquad (9)$$

where MW_i is the molecular weight of component i.

Refs. [1,2] show how a psychrometric chart for a system may be calculated using the virial equation and the enhancement factor to account for the non-idealities in the system. The psychrometric charts is constructed with temperature plotted on the x-axis and absolute humidity on the orthogonal y-axis. The saturation line that describes the boundary of the humidity chart is drawn by plotting the absolute humidity at saturation, H_s, as a function of temperature for a specified total pressure. Series of curves for constant relative humidity, constant specific volume and constant adiabatic saturation temperature may be generated by use of the equations presented.

The relative humidity, ϕ, is defined as the ratio of the mole fraction of the vapour component, x_V, in a given sample of the two-component mixture to the mole fraction, x_{V_s}, in a sample of the mixture which is saturated with the vapour component at that temperature. Thus,

$$\phi = \frac{x_V}{x_{V_s}} \qquad (10)$$

In order to construct the curves of constant relative humidity an expression is required which relates the absolute humidity to the relative humidity, temperature and total pressure. Shallcross [1] derives the equation:

$$H = \frac{H_s\phi(1-fP_V/P_T)}{1-\phi fP_V/P_T} \qquad (11)$$

To construct the constant relative humidity curves, the system pressure, P_T, is first specified. Then for a given value of ϕ, the variables f, H_s and P_V are calculated for varying temperatures. These values are then used in Eq. (11) to calculate the absolute humidity as a function of temperature. When plotted this data yields the constant relative humidity curves.

The specific volume of a humid mixture, ν, is defined as the volume of the mixture per unit mass of the dry gas:

$$\nu = \frac{\widehat{V}}{x_G MW_G} \qquad (12)$$

Applying this definition and using Eq. (1), Shallcross [1] shows how the curves of constant specific volume may be plotted for a given system pressure.

The wet bulb temperature is usually considered as the temperature measured by a cylindrical thermometer, the outside surface of which is kept wet with the liquid of the condensing component V. As the moist gas passes the thermometer some of the liquid evaporates resulting in a cooling effect that causes the temperature of the wet bulb thermometer to drop. The drier the gas, the greater the wet bulb depression. As the wet bulb temperature is a function of not only the dry bulb temperature and absolute humidity, but also such factors as the gas velocity past the thermometer, the diameter of the thermometer and the extent of radiative heat transfer, it is not possible to predict the wet bulb temperatures with precision. Consequently we choose to plot instead curves of constant adiabatic saturation temperature. It should be noted however that for the air–water system the curves of constant adiabatic saturation temperature coincide with curves of constant wet bulb temperature. This is because for the air–water system the Lewis number is equal to one.

For the conventional air–water system, ASHRAE [5] defines the adiabatic saturation temperature, T_{ad}, as the temperature at which water (liquid or solid), by evaporating into moist air at a given dry bulb temperature, T, and absolute humidity, H, can bring air to saturation adiabatically at the same temperature, T_{ad}, while the pressure P_T, is maintained constant. The adiabatic saturation temperature is also known as the thermodynamic wet bulb temperature.

For a given G–V system, it may be defined as the temperature at which component V, present as either a liquid or a solid, by evaporating into the moist gas mixture at a given dry bulb temperature, T, and absolute humidity, H, can bring that mixture to saturation adiabatically at the same temperature, T_{ad}, while the pressure, P_T, is maintained constant. The method used to plot the curves of constant adiabatic saturation temperature is described in more detail elsewhere [1,2].

The calculation and representation of the specific enthalpy of the gas mixture requires special attention. The specific of the two-component gas mixture is calculated by summing the ideal gas state enthalpy and the residual enthalpy:

$$\hat{h} = x_G\left(\hat{h}_{0G} + \int_{T_0}^{T} C_{P_{G'}}\,\mathrm{d}T\right) + x_V\left(\hat{h}_{0V} + \int_{T_0}^{T} C_{P_{V'}}\,\mathrm{d}T\right) + RT\left[\left(T\frac{\mathrm{d}B_m}{\mathrm{d}T} - B_m\right)\frac{1}{\hat{V}_m} + \left(\frac{T}{2}\frac{\mathrm{d}C_m}{\mathrm{d}T} - C_m\right)\frac{1}{\hat{V}_m^2}\right] \tag{13}$$

In this equation T_0 is the enthalpy datum temperature, C_{P_G} and C_{P_V} are the ideal gas heat capacity of the gas and vapour respectively, and, $\hat{h}_{0G}$ and $\hat{h}_{0V}$ are the enthalpy corrections for both components necessary to ensure that the enthalpy, $\hat{h}$, is in fact zero at the enthalpy datum condition.

Because of the nature of the equations governing the construction of the constant adiabatic saturation temperature curves, lines of constant gas mixture enthalpy will lie nearly parallel with the adiabatic saturation temperature curves. Rather than plotting two sets of curves having nearly the same slope, which would result in a chart difficult to read, the gas mixture enthalpy data is presented in a different form. An enthalpy deviation term, $\hat{h}_{\mathrm{dev}}$, is defined as being the difference between the true specific enthalpy of a gas mixture and the specific enthalpy of the gas saturated at its adiabatic saturation temperature:

$$\hat{h}_{\mathrm{dev}} = \hat{h} - \hat{h}_{S,\mathrm{as}} \tag{14}$$

When curves of constant enthalpy deviation are plotted on the psychrometric chart then the true specific enthalpy of a gas mixture can be determined by adding the enthalpy deviation for the point on the chart representing the mixture, to the enthalpy of the gas saturated at its adiabatic saturation temperature.

3. Chart preparation and production

Five psychrometric charts for ketone vapour in air were prepared based upon the above equations together with the physical property data presented in Appendix A. The five ketones are propanone (acetone), 2-butanone, 3-methyl-s-butanone, 3-pentanone and 2-hexanone. Each chart was prepared for a system pressure of 100 kPa.

To prepare each chart a FORTRAN program was written incorporating the equations and the physical property data for the particular ketone. When run the FORTRAN program generated an output file containing instructions to prepare the chart in the Postscript graphics language. When sent to a suitable Postscript laser printer the psychrometric charts presented in Figs. 1–5 are produced. The charts are printed on a printer having a resolution of 600 dots per inch (23.6 dots per mm). This allows the curves on the charts to be plotted with extreme precision. On a chart with a temperature range of 50 °C a plotting precision of 600 dots per inch on a standard A4 sheet is equivalent to placing a line with an accuracy of 0.01 °C.

The layout of Fig. 1 is typical of the psychrometric chart produced by the above procedure. Dry bulb temperature is plotted on the x-axis with absolute humidity plotted on the y-axis. The relative humidity, specific volume, adiabatic saturation temperature and enthalpy deviation curves are all plotted as functions of dry bulb temperature and absolute humidity. The layout of the chart is self-explanatory. The enthalpy datum condition for the ketone is taken as liquid ketone at its own vapour pressure at 0 °C. The datum condition for air is 0 °C.

The inclined scale for the enthalpy at saturation is slightly non-linear with units varying in size along the length of the scale. The scale is prepared by extrapolating the lines of constant adiabatic saturation temperature beyond the saturation curve to intersect the inclined scale. The values of enthalpy at saturation at each adiabatic saturation temperature then form the basis of the scale.

To illustrate the use of the charts, consider the propanone vapour–air system presented in Fig. 1. For a total system pressure of 100 kPa, if the dry bulb temperature is 22.0 °C and the adiabatic saturation temperature is 10.0 °C, then the chart may be used to determine the following:

- absolute humidity 0.035 (kg ketone vapour)·(kg dry air)$^{-1}$;
- dew point 8.7 °C;
- specific volume 0.991 m^3·(kg dry air)$^{-1}$;
- specific enthalpy 226 kJ·(kg dry air)$^{-1}$.

4. Discussion

The position of the saturation curve and hence the shape of the psychrometric chart is influenced by the magnitude of the enhancement factor with temperature. Fig. 6 shows the variation in the enhancement factor with temperature for the five ketone vapours in air at 100 kPa. In all cases the enhancement factor falls in the range, $1.019 < f < 1.030$.

As presented in Eq. (8), the enhancement factor is the sum of fifteen terms. Analysis of the relative magnitudes of these terms show that just four terms dominate the sum, namely the first, third, fourth and fifth terms of the right-hand side of Eq. (8). Fig. 7 shows the values of these four terms in Eq. (8) for 3-pentanone vapour in air at 100 kPa. The behaviour of the four terms for 3-pentanone are typical for the five ketones considered in this present study.

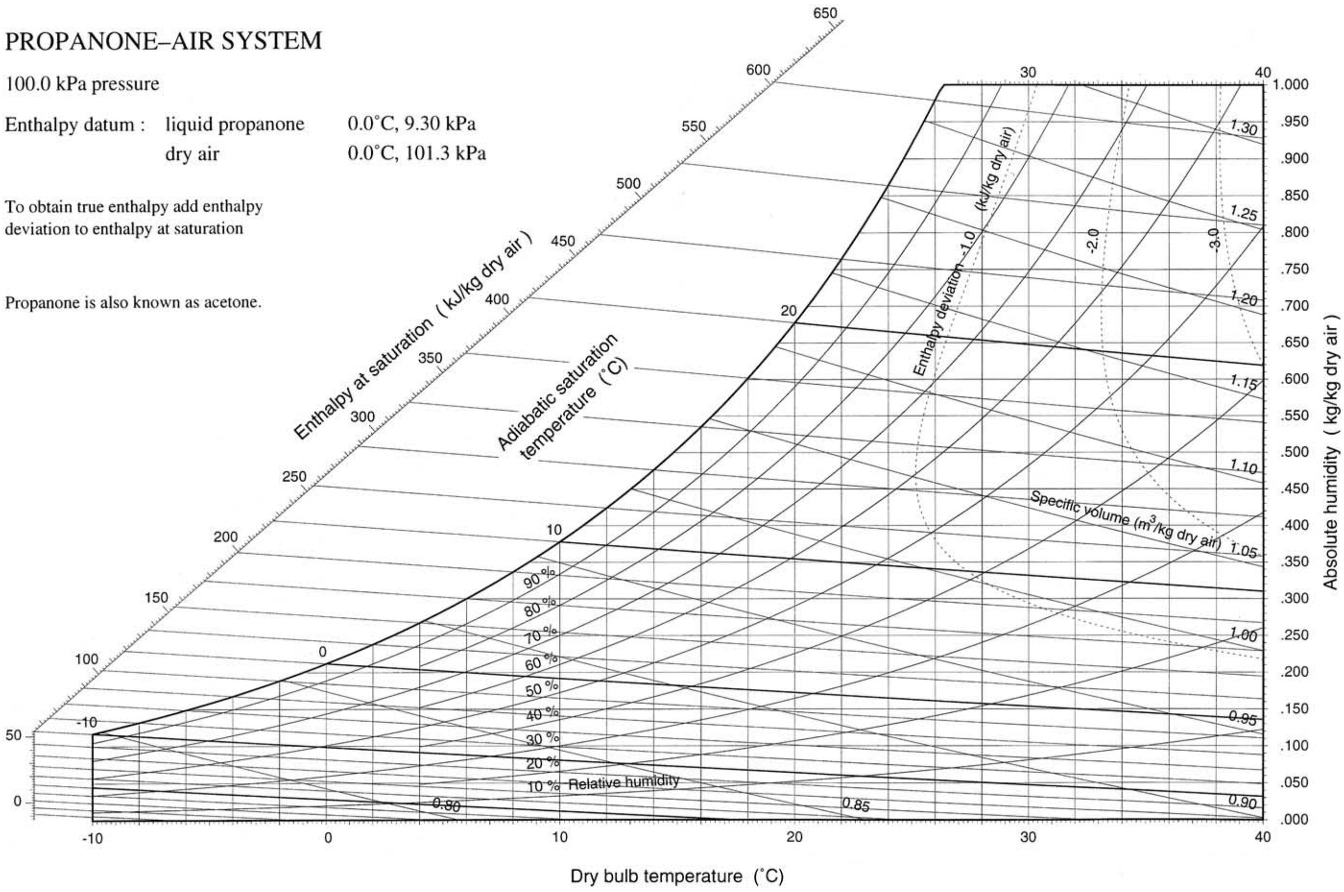

Fig. 1. Psychrometric chart for the propanone–air system at 100.0 kPa.

In the light of this analysis the expression for $\ln f$ in Eq. (8) may be approximated by the following equation without significant loss of accuracy:

$$\ln f = \left[\frac{(1+\kappa P_V)(P_T - P_V) - \frac{1}{2}\kappa(P_T^2 - P_V^2)}{RT}\right]\widehat{V}_{V_c} + \frac{x_{G_s}^2 P_T}{RT}B_{GG} - \frac{2x_{G_s}^2 P_T}{RT}B_{GV} - \left[\frac{P_T - P_V - x_{G_s}^2 P_T}{RT}\right]B_{GG} \qquad (15)$$

Using this approximation for f results in an error of less than 0.1% compared to the value for f calculated using Eq. (8). Note that the five psychrometric charts presented in this paper were developed using Eq. (8) rather than Eq. (15) to calculate the enhancement factor, f. In the above formulation neither the Henry's law constant, k_H, nor any of the third virial coefficients appear.

Whilst experimental data is not available to test the predictions made for charts prepared for water vapour in Martian atmosphere, the charts prepared for the water–air system using the same technique [2] agree extremely well with the widely accepted standard charts published by ASHRAE [5].

5. Concluding remarks

Using published physical property data and correlations, and equations developed earlier by the author, a series of high-precision psychrometric charts have been constructed for five different ketone vapours in air. The fact that the model produces a chart in very close agreement to the widely accepted standard psychrometric chart for the water–air system supports the notion that the reliability of the charts produced are high.

Appendix A. Physical property data

With the exception of the Henry's law constants and the isothermal compressibilities all the ketone physical property data required to prepare the charts are taken from a single source [6]. This is done to ensure consistency.

Molecular weights, critical point data and the acentric factor

A number of the correlations used to estimate the required parameters call for information concerning the critical point and the acentric factor for each component. This information

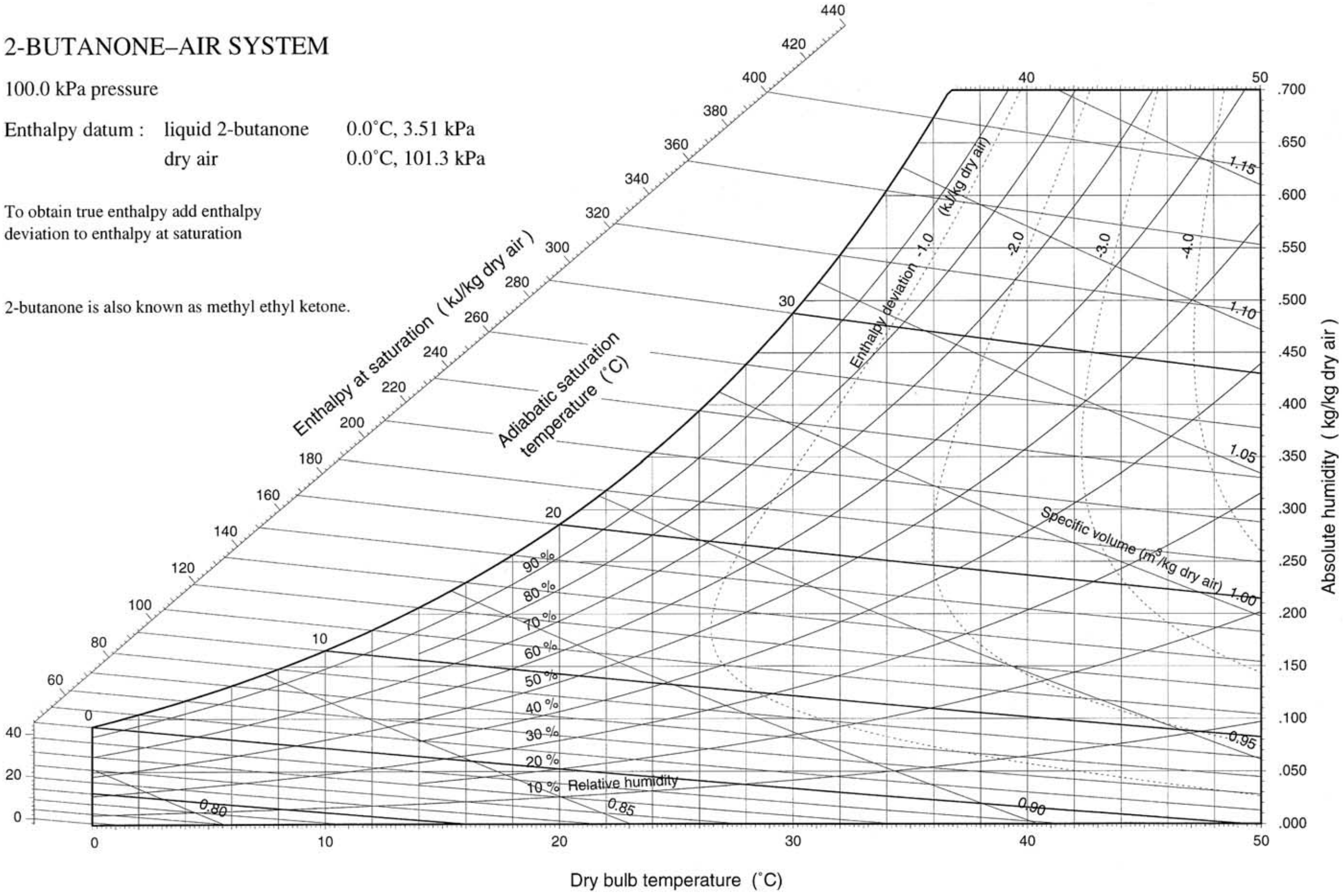

Fig. 2. Psychrometric chart for the 2-butanone–air system at 100.0 kPa.

Table 1
Molecular weight, critical point and the acentric factor data

Component	MW	T_c [K]	P_c [MPa]	$\widehat{V}_c$ [$\text{m}^3\cdot\text{kmol}^{-1}$]	Z_c	ω
Nitrogen	28.014	126.20	3.3939	0.0886	0.287	0.045
Oxygen	31.999	154.58	5.0764	0.0498	0.197	0.019
Argon	39.948	150.86	4.8980	0.0746	0.291	0.000
Carbon dioxide	44.010	304.20	7.3815	0.0929	0.271	0.231
Neon	20.180	44.40	2.6530	0.0417	0.300	−0.041
Air	28.965	132.43	3.9687	0.0795	0.290	0.0392
Propanone	58.080	508.20	4.7015	0.209	0.233	0.3064
2-butanone	72.107	535.50	4.1543	0.267	0.249	0.3241
3-methyl-2-butanone	86.134	553.40	3.8000	0.310	0.256	0.3208
3-pentanone	86.134	560.95	3.7400	0.336	0.269	0.3448
2-hexanone	100.161	587.61	3.2870	0.378	0.254	0.3846

is presented in Table 1. As air is a mixture, the data relating to its constitutive components is presented.

Since some of the correlations that follow require single values of T_c, P_c, $\widehat{V}_c$, Z_c and ω for air these must be calculated. Kay's rule is used to calculate a pseudo-critical temperature T_c' for air:

$$T_c' = \sum_i x_i T_{c_i} \tag{A.1}$$

summed over all components.

For the pseudo-critical pressure, P_c', the following equation is used [7]:

$$P_c' = \frac{R(\sum_i x_i Z_{c_i})T_c'}{\sum_i x_i \widehat{V}_{c_i}} \tag{A.2}$$

The acentric factor for air is simply taken as

$$\omega' = \sum_i x_i \omega_i \tag{A.3}$$

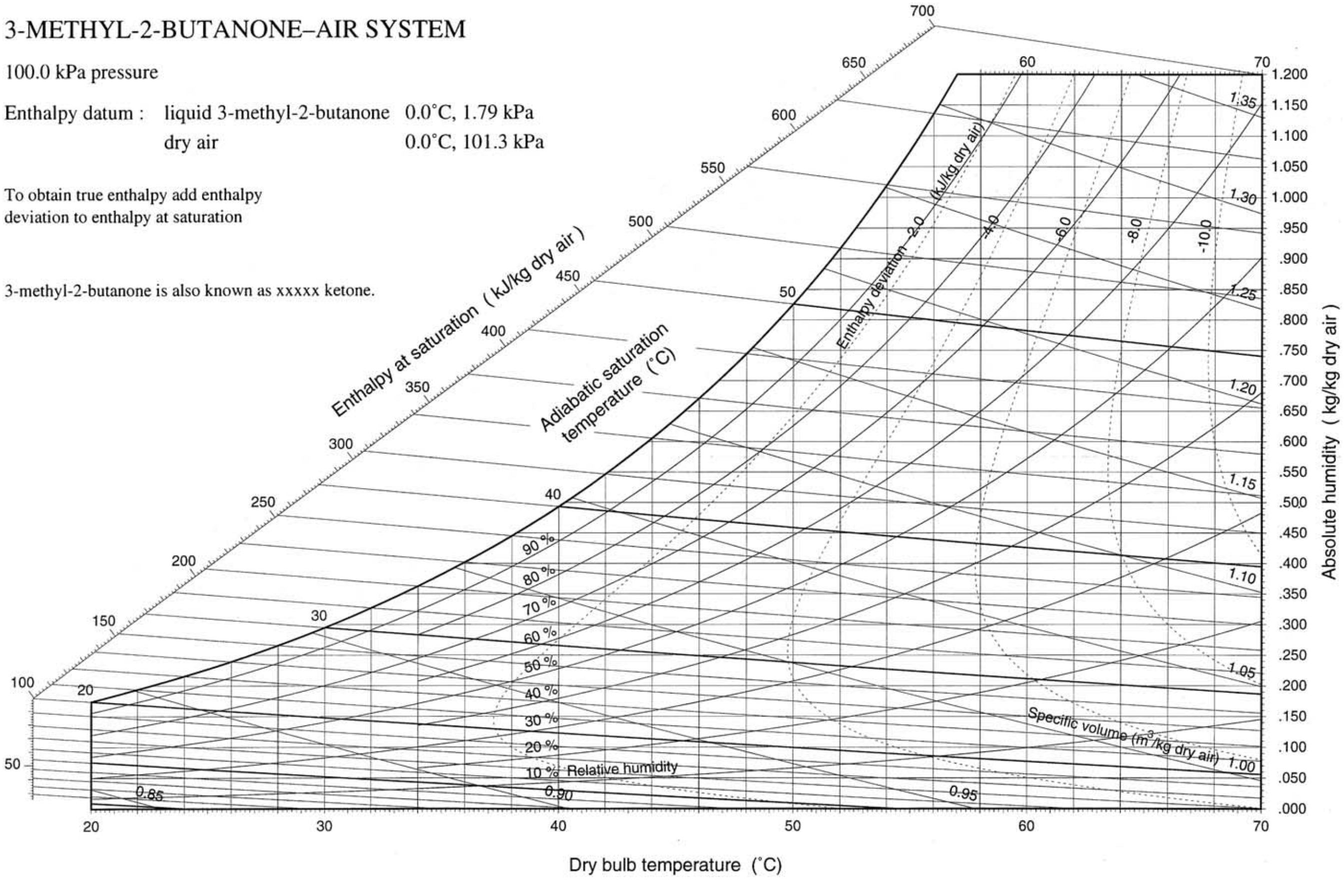

Fig. 3. Psychrometric chart for the 3-methyl-2-butanone–air system at 100.0 kPa.

The pseudo-critical compressibility factor, Z'_c, is calculated from

$$Z'_c = Z^{(0)} + \omega' Z^{(1)} \tag{A.4}$$

where $Z^{(0)} = 0.2901$ and $Z^{(1)} = -0.0879$ at the critical point [8].

The pseudo-critical volume, $\widehat{V}_c$, is calculated from

$$\widehat{V}'_c = \frac{Z'_c R T'_c}{P'_c} \tag{A.5}$$

The composition of dry, clean air on a molar basis is assumed to be: 78.0849% nitrogen, 20.9479% oxygen, 0.9340% argon, 0.0314% carbon dioxide, and 0.0018% neon [5].

So, for dry air, $MW = 28.965$, $T'_c = 132.43$ K, $P'_c = 3.9687$ MPa, $\widehat{V}_c = 0.07953\ \mathrm{m^3 \cdot kmol^{-1}}$, $Z'_c = 0.2896$ and $\omega' = 0.0392$.

Second virial coefficient

Hyland and Wexler [4] present a correlation for the second virial coefficient for dry air as a function of absolute temperature:

$$B_{AA} = 34.9568 - \frac{0.668772 \times 10^4}{T} - \frac{0.210141 \times 10^7}{T^2} + \frac{0.924746 \times 10^8}{T^3} \tag{A.6}$$

where T is expressed in Kelvin and B_{AA} is expressed in $\mathrm{cm^3 \cdot mol^{-1}}$.

For the ketones Daubert et al. [6] recommend the use of an equation of the form:

$$B_{VV} = c_1 + \frac{c_2}{T} + \frac{c_3}{T^3} + \frac{c_4}{T^8} + \frac{c_5}{T^9} \tag{A.7}$$

where T is expressed in Kelvin and B_{VV} is expressed in $\mathrm{cm^3 \cdot mol^{-1}}$. The coefficients for the ketones are presented in Table 2 and have been taken from Daubert et al. [6] after unit conversion.

Second virial cross coefficients

The second virial cross coefficients are estimated using the empirical correlation [9]:

$$B_{ij} = \widehat{V}_{c_{ij}} \left[c_1 + \omega_{ij} c_2 + \frac{c_3 + \omega_{ij} c_4}{T_{r_{ij}}} + \frac{c_5 + \omega_{ij} c_6}{T^2_{r_{ij}}} + \frac{c_7 + \omega_{ij} c_8}{T^6_{r_{ij}}} \right] \tag{A.8}$$

where the critical properties $T_{c_{ij}}$, $\widehat{V}_{c_{ij}}$ and ω_{ij} are defined as:

$$T_{c_{ij}} = \sqrt{T_{c_i} T_{c_j}} \tag{A.9}$$

$$\widehat{V}_{c_{ij}} = \left(\frac{\widehat{V}^{1/3}_{c_i} + \widehat{V}^{1/3}_{c_j}}{2} \right)^3 \tag{A.10}$$

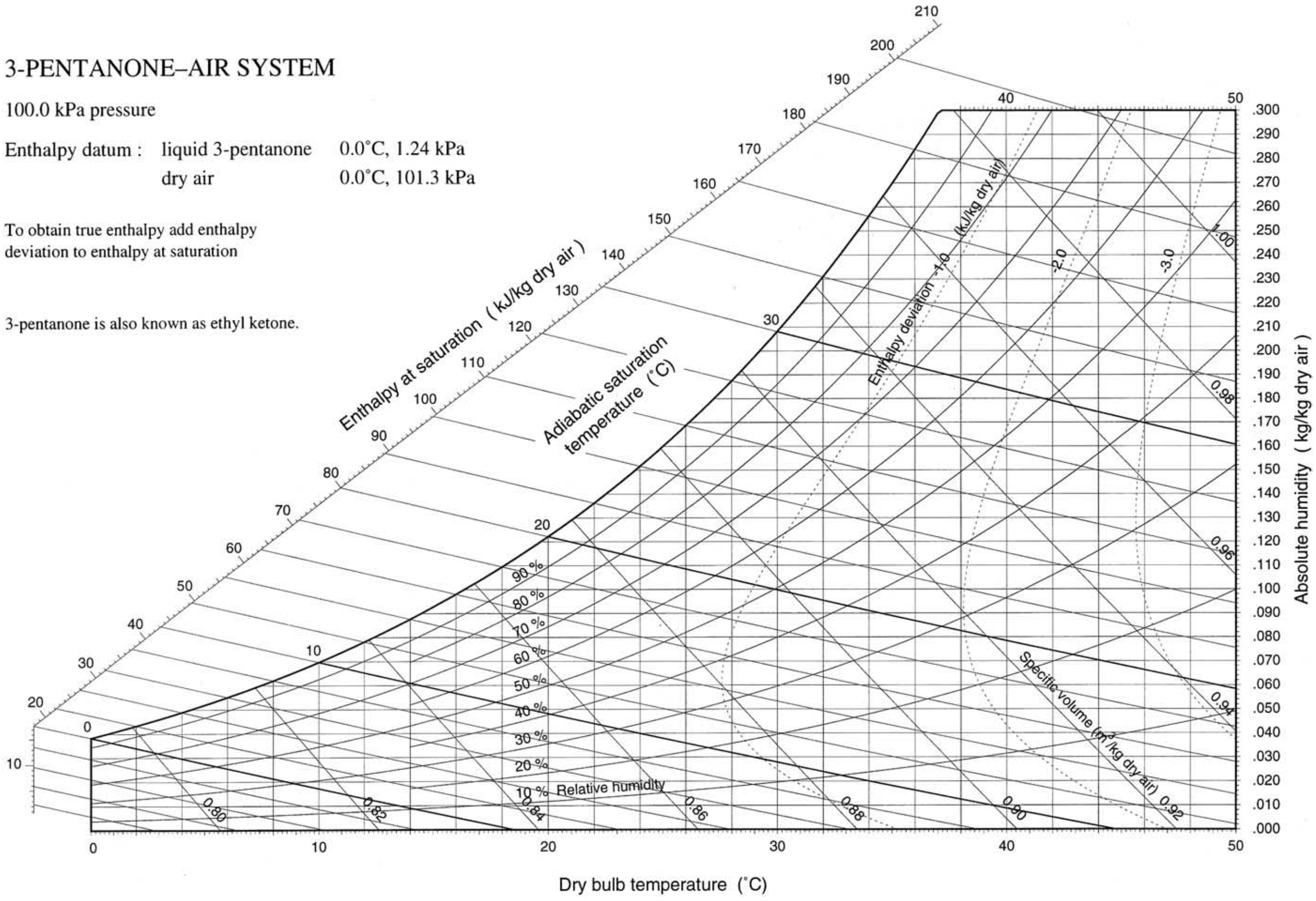

Fig. 4. Psychrometric chart for the 3-pentanone–air system at 100.0 kPa.

Table 2
Second virial coefficient parameters for Eq. (A.7)

Component	c_1	c_2	c_3	c_4	c_5
Propanone	1.1070×10^{2}	-9.9200×10^{4}	-3.0540×10^{10}	9.8900×10^{21}	-1.6454×10^{25}
2-butanone	9.0100×10^{1}	-8.6700×10^{4}	-6.0500×10^{10}	3.4650×10^{23}	-1.0330×10^{26}
3-methyl-2-butanone	1.6000×10^{2}	-1.3010×10^{5}	-4.9140×10^{10}	6.1000×10^{20}	-2.9330×10^{25}
3-pentanone	1.9680×10^{2}	-2.1873×10^{5}	-4.5060×10^{10}	-1.5690×10^{23}	1.9653×10^{25}
2-hexanone	2.4931×10^{2}	-2.8704×10^{5}	-5.8288×10^{10}	-2.8661×10^{23}	4.2633×10^{25}

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{A.11}$$

In Eq. (A.8),

$c_1 = 0.442259$, $c_2 = 0.725650$

$c_3 = -0.980970$, $c_4 = 0.218714$

$c_5 = -0.611142$, $c_6 = -1.24976$

$c_7 = -0.11515624$, $c_8 = -0.189187$

Third virial coefficients

A correlation for the third virial coefficient for dry air as a function of absolute temperature is (Hyland and Wexler):

$$C_{AAA} = 1.25975 \times 10^{3} - \frac{1.90905 \times 10^{5}}{T} + \frac{6.32467 \times 10^{7}}{T^{2}} \tag{A.12}$$

where C_{AAA} is expressed in $\mathrm{cm^6 \cdot mol^{-2}}$.

The generalised empirical correlation of Orbey and Vera (1983) is used to estimate the third virial coefficients:

$$\frac{C P_c^2}{(RT)^2} = g_1 + \omega g_2 \tag{A.13}$$

where C is the third virial coefficient, P_c is the critical pressure, T_c is the critical temperature, R is the Universal gas constant, ω is the acentric factor, and g_1 and g_2 are both functions of the reduced temperature:

$$g_1 = 0.01407 + \frac{0.02432}{T_r^{2.8}} - \frac{0.00313}{T_r^{10.5}} \tag{A.14}$$

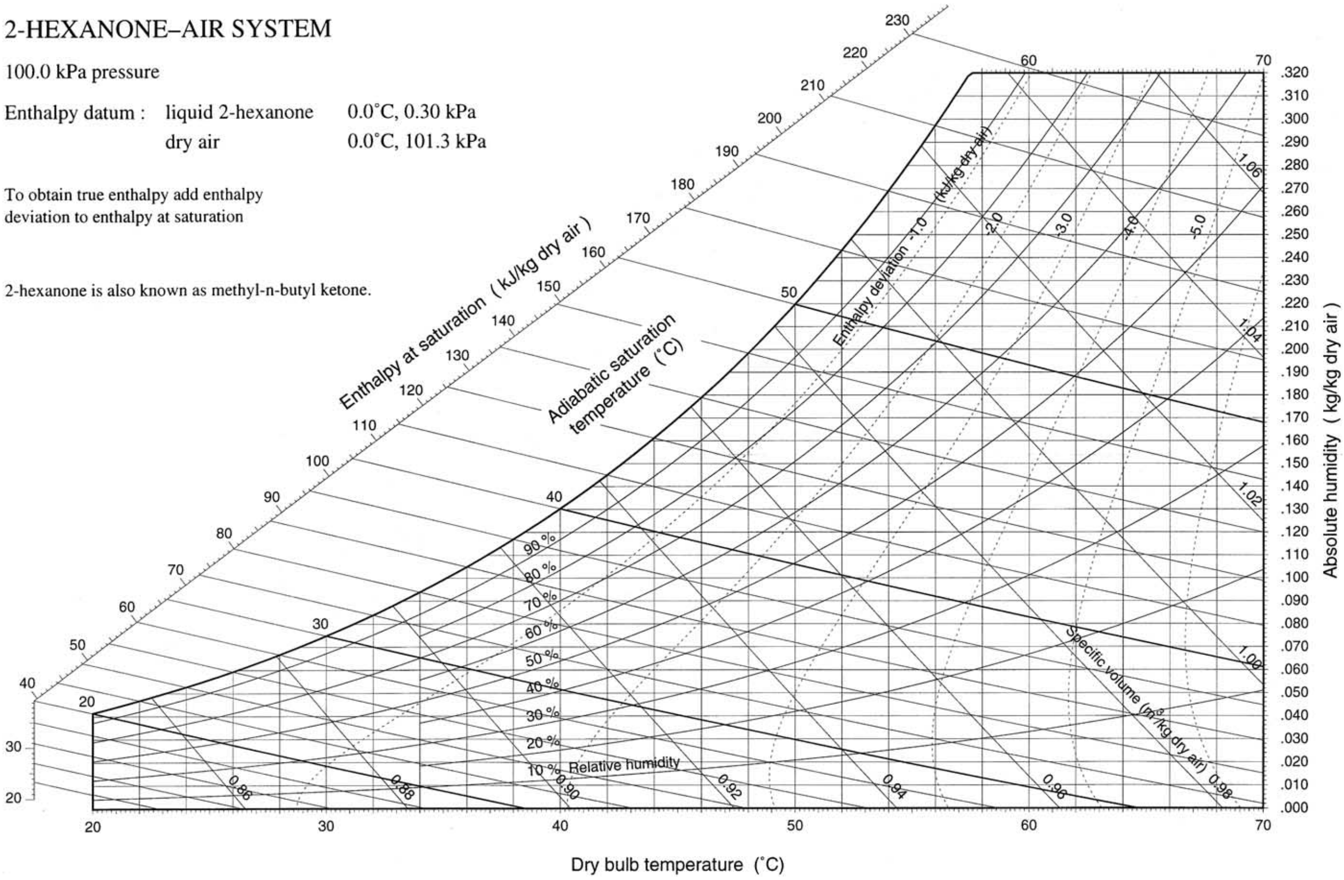

Fig. 5. Psychrometric chart for the 2-hexanone–air system at 100.0 kPa.

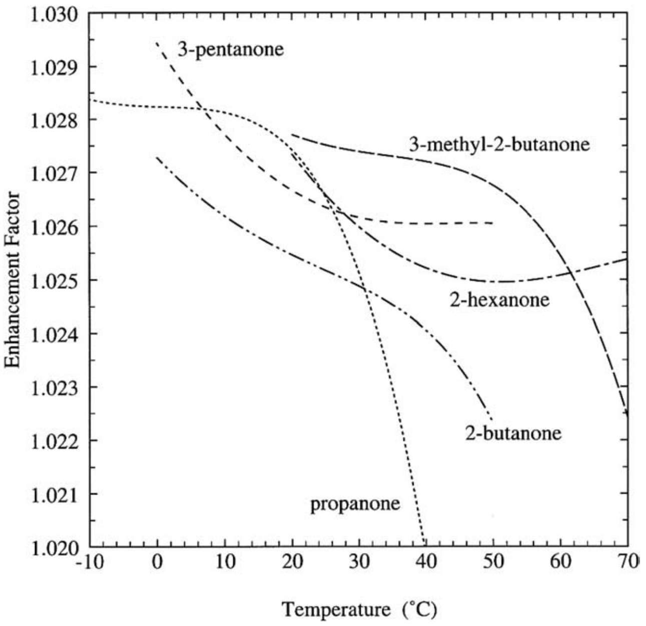

Fig. 6. Enhancement factor for the five ketones as a function of temperature.

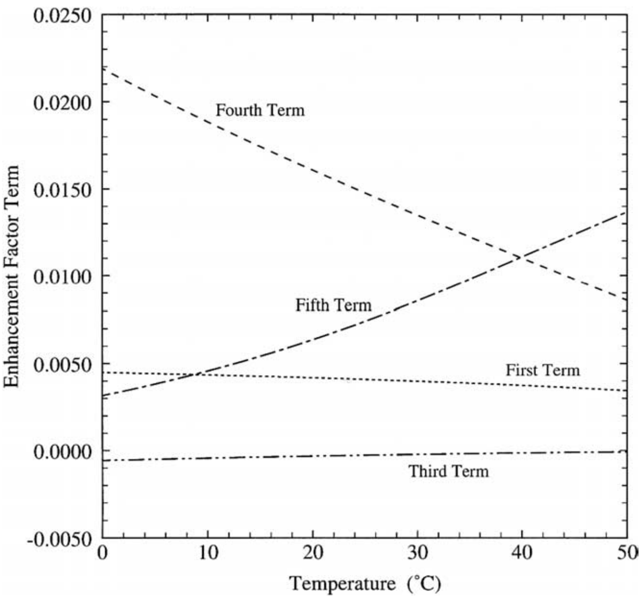

Fig. 7. Comparison of the four terms that dominate Eq. (8) for the enhancement factor. 3-pentanone in air system at 100 kPa.

$$g_2 = -0.02676 + \frac{0.01770}{T_r^{2.8}} + \frac{0.040}{T_r^{3.0}} - \frac{0.003}{T_r^{6.0}} - \frac{0.00228}{T_r^{10.5}} \qquad \text{(A.15)}$$

Third virial cross coefficients

The two third virial cross coefficients for the each of the systems, C_{iij} and C_{ijj}, are estimated using the empirical correlation shown below [10]. Brugge et al. [11] found this correlation to be good for estimating for cross coefficients for three different systems. The correlation is

$$C_{ijk} = (C_{ij}C_{ik}C_{jk})^{1/3} \tag{A.16}$$

where

$$C_{ij} = \left(\frac{RT_{c_{ij}}}{P_{c_{ij}}}\right)(g_1 + \omega_{ij}g_2) \tag{A.17}$$

and g_1 and g_2 are both functions of $T_{r_{ij}}$ defined in Eqs. (A.14) and (A.15). The cross critical temperature and cross acentric factor are defined as in Eqs. (A.9) and (A.11), respectively. The cross critical pressure is defined as

$$\begin{aligned} P_{c_{ij}} &= 4(Z_{c_i} + Z_{c_j})T_{c_{ij}} \\ &\quad \times \left[\left(\frac{Z_{c_i}Z_{c_j}}{P_{c_i}}\right)^{1/3} + \left(\frac{Z_{c_i}Z_{c_j}}{P_{c_j}}\right)^{1/3}\right]^3 \end{aligned} \tag{A.18}$$

Vapour pressure

Daubert et al. [6] recommend the use of an equation of the following form to estimate vapour pressures for ketones:

$$P_V = \exp\left(c_1 + \frac{c_2}{T} + c_3\ln(T) + c_4T^{c_5}\right) \tag{A.19}$$

where P_V is the vapour pressure expressed in Pa, and T is the absolute temperature expressed in Kelvin. Values for the five parameters for Eq. (A.19) are presented in Table 3.

Isothermal compressibility

Isothermal compressibility may be related to temperature by a correlation of the form

$$\kappa = (c_1 + c_2t) \times 10^{-10} \tag{A.20}$$

where κ is the isothermal compressibility expressed in Pa^{-1}, and t is the temperature expressed in °C. When the data for propanone presented by McGowan [12] is regressed we find that $c_1 = 9.6937$ and $c_2 = 0.12964$. As data for the other ketones is unavailable we will assume that the isothermal compressibility is the same for all the ketones in the present study.

Molar volume of condensed phase

Daubert et al. [6] present a correlation for the density of the liquid ketones. From this an expression for the molar volume of the liquid ketones may be derived:

$$\widehat{V}_{V_c} = \frac{c_2^{(1+(1-T/c_3)^{c_4})}}{c_1} \tag{A.21}$$

where $\widehat{V}_{V_c}$ is the molar volume of the liquid ketone expressed in $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$, and T is the absolute temperature in Kelvin. Values for the four parameters for Eq. (A.21) are presented in Table 4.

Henry's law constants

The solubility of the air in the liquid ketones is considered in Eq. (8) by making use of Henry's law constants. Henry's law constant for a mixture may be calculated from the composition of the gas and the values of the Henry's law constants for the individual components:

$$\frac{1}{k_H^{\mathrm{Air}-V}} = \sum_j \frac{x_j}{k_H^{j-V}} \tag{A.22}$$

where $k_H^{\mathrm{Air}-V}$ is the Henry's law constant for air in liquid V, x_j is the mole fraction of component j in the dry gas mixture and k_H^{j-V} is the Henry's law constant for gas component j in liquid V.

Thus, Henry's law constant for air in liquid V is

Table 3
Vapour pressure parameters for Eq. (A.19)

Component	c_1	c_2	c_3	c_4	c_5
Propanone	7.0720×10^1	-5.6850×10^3	-7.3510	6.3000×10^{-6}	2.00
2-butanone	1.1474×10^2	-7.1300×10^3	-1.5184×10^1	1.7234×10^{-2}	1.00
3-methyl-2-butanone	4.5242×10^1	-5.3244×10^3	-3.2551	3.0363×10^{-18}	6.00
3-pentanone	4.4286×10^1	-5.4151×10^3	-3.0913	1.8580×10^{-18}	6.00
2-hexanone	1.0744×10^2	-8.5286×10^3	-1.2679×10^1	8.4606×10^{-6}	2.00

Table 4
Molar volume of condensed phase parameters for Eq. (A.21)

Component	c_1	c_2	c_3	c_4
Propanone	1.2298×10^{-3}	2.5760×10^{-1}	5.0820×10^2	2.9903×10^{-1}
2-butanone	9.3300×10^{-4}	2.5140×10^{-1}	5.3550×10^2	2.8570×10^{-1}
3-methyl-2-butanone	8.6567×10^{-4}	2.6836×10^{-1}	5.5340×10^2	2.8364×10^{-1}
3-pentanone	7.1811×10^{-4}	2.4129×10^{-1}	5.6095×10^2	2.7996×10^{-1}
2-hexanone	6.7816×10^{-4}	2.5634×10^{-1}	5.8761×10^2	2.8365×10^{-1}

$$\frac{1}{k_H^{\mathrm{Air}-V}} = \frac{0.780849}{k_H^{\mathrm{N_2}-V}} + \frac{0.209479}{k_H^{\mathrm{O_2}-V}} + \frac{0.009340}{k_H^{\mathrm{Ar}-V}} + \frac{0.000314}{k_H^{\mathrm{CO_2}-V}} + \frac{0.000018}{k_H^{\mathrm{Ne}-V}} \tag{A.23}$$

Based upon the data and regressions presented in the volumes of the solubility data series [14–18], Henry's law constants may be related to temperature through equations of the form:

$$k_H^{j-V} = \frac{1}{\exp(c_1 + c_2/T + c_3\ln(T))} \tag{A.24}$$

where k_H^{j-V} is expressed in atm and T is expressed in Kelvin. From the limited data available the values for the three parameters are presented in Table 5. The values for the gas component–liquid systems for which data is not available, have been estimated by the author.

Ideal gas heat capacity

Daubert et al. [6] recommend the use of an equation of the following form to estimate the ideal gas heat capacity of the ketones and the gaseous components of the dry air:

$$C_P = c_1 + c_2\left[\frac{c_3}{T\sinh(c_3/T)}\right]^2 + c_4\left[\frac{c_5}{T\cosh(c_5/T)}\right]^2 \tag{A.25}$$

where C_P is the heat capacity expressed in J·mol^{-1}·K^{-1} and T is the absolute temperature expressed in Kelvin. The parameters for the dry air components as well as the ketones presented in Table 6 are from Daubert et al. after unit conversion.

Table 5
Henry's law constant parameters for Eq. (A.24)

Ketone	Gas	c_1	c_2	c_3	Source
Propanone	N_2	−22.1720	377.545	2.34933	Ref. [16]
	O_2	−26.2178	718.725	2.936	Ref. [15]
	Ar	−6.2389	−228.966	0	Ref. [14]
	CO_2	−10.5990	1980.7	−0.0028	Ref. [18]
	Ne	−4.6937	−1211.40	0	Ref. [13]
2-butanone	N_2	−7.32	0	0	estimated
	O_2	−6.88	0	0	Ref. [15]
	Ar	−6.61	0	0	estimated
	CO_2	−3.96	0	0	Ref. [18]
	Ne	−8.52	0	0	estimated
3-methyl-2-butanone	N_2	−7.32	0	0	estimated
	O_2	−6.88	0	0	estimated
	Ar	−6.71	0	0	estimated
	CO_2	−3.95	0	0	estimated
	Ne	−8.62	0	0	estimated
3-pentanone	N_2	−7.32	0	0	estimated
	O_2	−6.88	0	0	estimated
	Ar	−6.71	0	0	estimated
	CO_2	−3.94	0	0	Ref. [18]
	Ne	−8.62	0	0	estimated
2-hexanone	N_2	−7.22	0	0	estimated
	O_2	−6.78	0	0	Ref. [15]
	Ar	−6.60	0	0	estimated
	CO_2	−3.95	0	0	Ref. [18]
	Ne	−8.52	0	0	estimated

Table 6
Ideal gas heat capacity parameters for Eqs. (A.25) and (A.26)

Component	c_1	c_2	c_3	c_4	c_5
Nitrogen	2.9105×10^{1}	8.6149	1.7016×10^{3}	1.0347×10^{-1}	9.0779×10^{2}
Oxygen	2.9103×10^{1}	1.0040×10^{1}	2.5265×10^{3}	9.3560	1.1538×10^{3}
Argon	2.0786×10^{1}	0	0	0	0
Carbon dioxide	2.9370×10^{1}	3.4540×10^{1}	-1.4280×10^{3}	2.6400×10^{1}	5.8800×10^{2}
Neon	2.0786×10^{1}	0	0	0	0
Propanone	4.8120×10^{1}	1.6440×10^{2}	1.2500×10^{3}	7.1700×10^{1}	-5.2440×10^{2}
2-butanone	7.8400×10^{1}	2.1032×10^{2}	1.5488×10^{3}	1.1855×10^{2}	6.9300×10^{2}
3-methyl-2-butanone	1.5914×10^{2}	1.7640×10^{2}	1.2076×10^{3}	-4.0740×10^{4}	1.0503×10^{1}
3-pentanone	9.6896×10^{1}	2.4907×10^{2}	1.4177×10^{3}	1.3010×10^{2}	6.4670×10^{2}
2-hexanone	1.0940×10^{2}	1.8070×10^{2}	6.8900×10^{2}	1.4740×10^{2}	1.7720×10^{3}

Table 7
Latent heat of vaporisation parameters for Eq. (A.27)

Component	c_1	c_2	c_3	c_4
Propanone	4.9170×10^{-7}	1.0360	−1.2940	6.7200×10^{-1}
2-butanone	5.1400×10^{-7}	7.5450×10^{-1}	-5.9500×10^{-1}	2.3300×10^{-1}
3-methyl-2-butanone	4.7075×10^{-7}	3.3601×10^{-1}	0	0
3-pentanone	5.2359×10^{-7}	4.0465×10^{-1}	0	0
2-hexanone	5.6231×10^{-7}	3.8207×10^{-1}	0	0

Table 8
Liquid phase heat capacity parameters for Eq. (A.29)

Component	c_1	c_2	c_3	c_4	c_5
Propanone	1.3560×10^{5}	-1.7700×10^{2}	2.8370×10^{-1}	6.8900×10^{-4}	0
2-butanone	1.3230×10^{5}	2.0087×10^{2}	-9.5970×10^{-1}	1.9533×10^{-3}	0
3-methyl-2-butanone	1.9117×10^{5}	-3.3104×10^{2}	9.8445×10^{-1}	0	0
3-pentanone	1.9302×10^{5}	-1.7643×10^{2}	5.6690×10^{-1}	0	0
2-hexanone	2.0825×10^{5}	-1.0747×10^{2}	2.0620×10^{-1}	7.0293×10^{-4}	0

To obtain an expression for specific enthalpy equation (A.25) is integrated with respect to temperature:

$$\hat{h} = c_1(T - T_{\text{datum}}) + c_2c_3\left[\coth\left(\frac{c_3}{T}\right) - \coth\left(\frac{c_3}{T_{\text{datum}}}\right)\right] - c_4c_5\left[\tanh\left(\frac{c_5}{T}\right) - \tanh\left(\frac{c_5}{T_{\text{datum}}}\right)\right] \quad \text{(A.26)}$$

Here, $\hat{h}$ is the ideal enthalpy of the gas at temperature T relative to an enthalpy datum condition of T_{datum}.

Latent heat of vaporisation

The latent heat of vaporisation is estimated using an equation of the form [6]:

$$\lambda = c_1(1 + T_r)^{(c_2 + c_3T_r + c_4T_r^2)} \quad \text{(A.27)}$$

where λ is the latent heat of vaporisation expressed in J·kmol^{-1}, and T is the absolute temperature expressed in Kelvin. Values for the five parameters for Eq. (A.27) are presented in Table 7.

Condensed phase enthalpy

An ability to predict the enthalpy of the liquid ketones is essential to determine the location of the curves of constant adiabatic saturation temperature as well as the enthalpy deviation curves. The heat capacity of the liquid ketones is estimated using [6]:

$$C_{P_L} = c_1 + c_2T + c_3T^2 + c_4T^3 + c_5T^4 \quad \text{(A.28)}$$

where C_{P_L} is the heat capacity expressed in J·kmol^{-1}·K^{-1}, and T is the absolute temperature expressed in Kelvin. The parameters for the ketones presented in Table 8 are from Ref. [6] after unit conversion.

To obtain an expression for specific enthalpy equation (A.28) is integrated with respect to temperature:

Table 9
Enthalpy corrections for air and the ketones

Component	Enthalpy correction [J·mol^{-1}]
Air	8.138
Propanone	219.167
2-butanone	119.521
3-methyl-2-butanone	80.828
3-pentanone	40.473
2-hexanone	14.079

$$\hat{h}_f = c_1(T - T_{\text{datum}}) + c_2\left(T^2 - T_{\text{datum}}^2\right)/2 + c_3\left(T^3 - T_{\text{datum}}^3\right)/3 + c_4\left(T^4 - T_{\text{datum}}^4\right)/4 + c_5\left(T^5 - T_{\text{datum}}^5\right)/5 \quad \text{(A.29)}$$

Here $\hat{h}_f$ is the specific enthalpy of a liquid ketone at temperature T relative to a datum temperature of T_{datum}. The specific enthalpy is expressed in J·kmol^{-1}.

Enthalpy corrections

The enthalpy corrections, $\hat{h}'_{0G}$ and $\hat{h}'_{0V}$, are applied in Eq. (13) to ensure that the enthalpy calculated is zero at the enthalpy datum condition. For air, $\hat{h}'_{0G}$ is found from Eq. (13) by setting $x_G = 1$ (and hence $x_V = 0$), $T = T_0 = 273.15$ K and $P = 101.3$ kPa (the datum condition).

The datum condition for the ketone vapour is taken as liquid at $T = T_0 = 273.15$ K and its own vapour pressure. In Eq. (13), $x_V = 1$, $T = T_0 = 273.15$ K and $P = P_V$ at T_0. The enthalpy corrections for air and the ketones are presented in Table 9.

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