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# Procedure for Estimating the Effects of Impurities on Measured Vapor Pressures

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Abstract

A thermodynamic relationship is used to describe how the presence of an impurity affects measured vapor pressures by relating the effect to the distribution coefficient, *K*, of the impurity. In practical situations *K* is estimated simply by analysis with a gas chromatograph. A second relationship is used to describe how *K*, and thus the effect, varies with temperature. The effect of azeotropic behavior on the temperature variation is also considered. Several examples are given, including the systems $CH_2F_2$ + $CF_3CH_2F$ (HFC32 + HFC134a), $CF_3CHF_2$ + $CF_3CF_2Cl$ (HFC125 + HCFC115), $CHF_2CF_2CH_2F$ + $CF_3CF_2CF_2CH_2F$ (HFC245ca + HFC338mccq), and samples of $CF_3CH_2CF_3$ (HFC236fa) and n-heptane with impurities.

**Key Words** azeotrope, distribution coefficient, impurity, mixtures, vapor pressure

## Introduction

Today, many laboratories are equipped with apparatus capable of making highly precise measurements of such basic quantities as temperature and pressure. Nevertheless, when measured thermophysical properties from different laboratories are compared, the differences are often much larger than can be explained by the quality of the measuring devices. Nowhere is this phenomenon more apparent than in the measurement of vapor pressures of pure fluids. Differences between laboratories often result from the presence of impurities in the samples. Vapor pressure measurements are measurements along a phase boundary, and an impurity can displace that boundary. Problems caused by dissolved air are well known, and samples are often degassed by one of several means. However, other less volatile impurities, such as the byproducts of a synthesis, can also lead to inaccuracies in the measured vapor pressure.

Often, the apparatus required to remove these impurities (fractional distillation columns, preparative gas chromatographs, etc.) is not available. Even when the apparatus is available, the purification process itself may use up a significant portion of the available sample, and the amount left may not be sufficient to make the desired measurements. Thus we are motivated to consider corrections for the presence of impurities. Often these corrections may involve less time and effort than attempts at purification.

In an earlier work, Weber (1994a), one of us showed how even a very dilute air impurity can have a great effect on measured vapor pressures and calculated thermodynamic properties, especially at low reduced temperatures. In this work, we show how the effects of a dilute impurity of unknown identity can be described thermodynamically. We offer a simple procedure, requiring only a common laboratory gas chromatograph, to determine the necessary information to account for the effect of the impurity. In the last section, we show some examples from our own work, illustrating how the procedure is implemented.

## Thermodynamic relationships

In the apparatus most commonly used for vapor pressure measurements, the effect of a dilute impurity is proportional to the initial slope of the bubble curve for the mixture, either $(\partial P/\partial x_2)_T^\infty$ or $(\partial T/\partial x_2)_P^\infty$, where substance 2 is taken to be the impurity or solute, and the fluid of interest is taken to be substance 1 or the solvent. The superscript ∞ denotes the condition of infinite dilution of the solute.

Ebulliometers are often used to study the thermodynamics of binary mixtures through the determination of the activity coefficient of the solute at infinite dilution, $\gamma_2^\infty$. The working equation used, simplified by the deletion of fugacity coefficients and the Poynting correction, has the form, Gautreaux and Coates (1955), Thomas et al. (1982),

$$\gamma_2^\infty = (P_1^\sigma/P_2^\sigma)\left[1-(\Delta Z_{lv}/P_1^\sigma)(dP_1^\sigma/dT)(\partial T/\partial x_2)_P^\infty\right] \qquad \textbf{(1)}$$

where the $P_i^\sigma$ are the vapor pressures of the components, $\Delta Z_{lv} = Z'' - Z'$ for the solvent, $(\partial T/\partial x_2)_p^\infty$ is the measured quantity, $Z''$ is the compressibility factor of the saturated vapor, $P^\sigma/\rho''RT$, and $Z'$ is the compressibility factor for the saturated liquid phase, $P^\sigma/\rho'RT$. The expression for the distribution coefficient of the solute, $K_2 = y_2/x_2$, again simplified by the above mentioned deletions, is, Van Ness and Abbott (1982),

$$K_2^\infty = \gamma_2^\infty (P_2^\sigma/P_1^\sigma) \qquad \textbf{(2)}$$

When eqs.(1 and 2) are combined and rearranged, we obtain the simple result,

$$\delta P/P = (K_2^\infty - 1)x_2/\Delta Z_{lv} \qquad \textbf{(3)}$$

which gives the relative error in the measured vapor pressure due to an impurity of component 2 with a liquid-phase mole fraction $x_2$, when one measures the

boiling temperature of the mixture. This relationship also holds for static measurements, as when vapor pressures are measured in a *PVT* apparatus. In those cases where an ebulliometer is used to measure the condensation temperature of the system, analogous arguments show that the relative error is given by,

$$\delta P/P = K_2^{\infty}(K_2^{\infty} - 1)x_2/\Delta Z_{lv} \qquad \textbf{(4)}$$

If both the boiling and condensation temperatures were to be measured, their difference would be a measure of the concentration of impurities, and their near equality would be an indication of a high-purity sample.

In the event that the solute is a supercritical gas, eq.(2) would not apply. The appropriate relationship is,

$$K_2^{\infty} = k_{2H}/P_1^{\sigma} \qquad \textbf{(5)}$$

where $k_{2H}$ is the Henry's constant. However, this relationship also leads to eqs.(3) and (4).

Eqs.(3) and (4) show how the error depends on the relative volatility of the impurity. Eq.(4) shows that a non volatile impurity such as a salt or heavy component, for which $K_2^{\infty}$ is very small, has a very small effect on the condensation temperature. The equations also show that air, for which $K_2^{\infty}$ varies from about 10 to $10^3$ would have a tremendous effect, even in minute concentrations.

From the foregoing it is obvious that in order to estimate the effect of an impurity, a value for $K_2^{\infty}$ is required. A value can be obtained simply with an ordinary gas chromatograph, provided that it is operated under conditions which separate the components. With the two-phase sample contained in a storage cylinder, it is only necessary to measure the chromatograms of both phases. Then, for an impurity, $K_2^{\infty}$ is given by,

$$K_2^{\infty} = (a_2/\sum a_i)_v/(a_2/\sum a_i)_l \qquad \textbf{(6)}$$

where the $a_i$ are the peak areas for the components in the two phases. The response factors all cancel out. If the identity of the impurity is unknown, $x_2$ must be estimated from the relative peak areas in the liquid phase, and the uncertainty in this estimate of $x_2$ will probably be the largest source of uncertainty in $\delta P/P$. In the case that several impurities are present, eqs.(3) and (4) can be generalized by using the subscript *i* and summing the right-hand-sides over all impurities under the assumption that the effect of any one impurity is independent of the presence of the others.

Eqs.(3) - (5) provide a simple and relatively accurate way to correct vapor pressure measurements for the presence of impurities. However, three of the quantities used, $K_2^{\infty}$, $x_2$ and $\Delta Z_{lv}$, are temperature dependent. In order to avoid measuring them over a wide temperature range, it is necessary to estimate the form of their temperature dependence. The compressibility factors may be estimated as follows. For the liquid phase, except near the critical point, $Z' << Z''$, and an estimate for the density of the saturated liquid, $\rho'$, suffices,

$$\rho' = \rho_c + b\tau^{\beta} \qquad \textbf{(7)}$$

where $\tau = (T_c - T)/T_c$, and $\beta$ may be taken to have a value such as 1/3, 0.35, 0.375, etc. The coefficient *b* may be determined from one reliable liquid density value in the temperature range of interest. If the critical density, $\rho_c$, is not known, the Rackett equation (see Reid, Prausnitz and Poling (1986)) may be used in place of eq.(7).

For the vapor phase, an equation of state is needed to calculate $Z''$. We use the virial equation,

$$Z'' = 1 + B\rho'' + C(\rho'')^2 \qquad \textbf{(8)}$$

If the virial coefficients have not been measured, they may be estimated, Weber (1994b). The virial coefficients *B* and *C* provide adequate densities for reduced temperatures, $T_r = T/T_c$, up to about 0.9; for work closer to the critical temperature, a relationship with the form of eq.(7) should be used for the vapor.

The liquid-phase mole fraction of the impurity, $x_2$, also varies with temperature, and it differs from the (constant) overall mole fraction, $z_2$ (the mole fraction of the feed in the storage cylinder), in a manner given by the mass balance relationship,

$$x_2/z_2 = (1+f)/(1+K_2^{\infty}f) \qquad \textbf{(9)}$$

where $f = n_v/n_l$, the ratio of the number of moles of vapor to the number of moles of liquid. Thus, the temperature dependence of $x_2$ depends on the relative volatility of the impurity, on the geometry of the apparatus, and on the vapor pressure of the sample. In most cases at low to moderate pressures $f$ is much less than 1. However, at higher pressures it can become significant, and near the critical point it approaches the value unity. The vapor volume of the apparatus and the virial coefficients can be used in the estimation of $n_v$ at any temperature. The data from the gas chromatograph (usually from a sample at ambient temperature) can be used with eq.(9) to determine $z_2$, from which $x_2$ can be calculated for any temperature.

The temperature variation of the distribution coefficient, $K_2^{\infty}$, can be estimated with the relationships derived by Japas and Levelt-Sengers (1989), who studied the behavior of dilute solutes near the critical point of the solvent. They showed that over a fairly wide range of temperature $K_2^{\infty}$ follows the relationship,

$$T \ln K_2^{\infty} \propto (\rho' - \rho_c) \qquad \textbf{(10)}$$

where the densities are values for the solvent. $K_2^{\infty}$ can be expressed as a function of temperature with the aid of eq.(7),

$$K_2^{\infty} = \exp(B(T_c/T)\,\tau^{\beta}) \qquad \textbf{(11)}$$

The coefficient ***B*** is determined from the gas chromatograph analyses. Eq.(11)

is used to calculate $K_2^\infty$ in eqs.(3,4,9). For work in the critical region, it is important that $K_2^\infty \rightarrow 1$ with the same behavior as $\Delta Z_{lv} \rightarrow 0$.

## Comparison with experiment

Eqs.(3) and (4) are thermodynamically exact. However, eqs.(10) and (11) were derived for the conditions of the critical region. Their use elsewhere can only be justified by comparison with experiment. Japas and Levelt-Sengers showed that eq.(10) holds very well for mixtures of CO + $C_6H_6$ for reduced temperatures down to 0.85. Weber (1989) showed that the equation also holds for mixtures of $CF_3Cl$ with n-$C_4H_{10}$ and with i-$C_4H_{10}$ for reduced temperatures down to 0.7, the lower limit of the data. Additional confirmations have been given by Alvarez et al. (1994) for several aqueous systems, and by Harvey et al. (1990) for one aqueous and one nonaqueous system.

Weber and Silva (1996) used a comparative ebulliometer to determine $K_2^\infty$ for mixtures of $CH_2F_2$ + $CF_3CH_2F$ (HFC32 + HFC134a) at 260, 280, and 300 K. Figure 1 shows the results plotted in a form suggested by eq.(11). The experimental $K_2^\infty$ agree with the equation with a fractional r.m.s. deviation of about 0.065, which is slightly more than their estimated uncertainty. The figure shows that both more volatile and less volatile impurities obey eq.(11).

The second example is for a $C_2F_5Cl$ (HCFC115) impurity in a sample of $C_2HF_5$ (HFC125), taken from Weber and Silva (1994). This mixture does not obey eq.(11) because it forms an azeotrope at temperatures below about 280 K. The azeotropic composition is very near the pure HFC125 end of the dew/bubble curves. Weber and Silva (1994) added a second term to the right hand side of eq.(11), of the form, $+b(T_c - T)^n$ with $b$ being a fitted parameter, and n $\approx$ 3. Figure 2 shows the resulting curve. At higher temperatures the curve follows the typical behavior for a less volatile impurity, while at lower temperatures it accomodates the onset of azeotropy. This example shows that, if an azeotrope with a less-volatile impurity is suspected, then it is necessary to measure $K_2^\infty$ at more than one temperature in order to determine its complete temperature dependence.

The situation shown in Figure 2 often occurs because the azeotropic composition usually migrates toward the more volatile component with increasing temperature. Often the $K_2^\infty$ at the other end of the bubble curve (more volatile impurity in a less volatile solvent) is unaffected by this azeotropic

behavior.

Exactly this situation is illustrated by the behavior in the next example, an azeotropic mixture of 1,1,2,2,3-pentafluoropropane + 1,1,1,2,2,3,3,4-octofluorobutane (HFC245ca + HFC338mccq) studied by Weber and Defibaugh (1997) with an ebulliometer and shown in Figure 3. Figure 3 shows the temperature dependence of both $K^{\infty}$ in the experimental temperature range, 300 K to 375 K. In this mixture the azeotropic composition approaches the pure HFC245ca at a temperauture of about 385 K (abscissa ≈ 0.48 in Figure 3). Therefore, the $K_2^{\infty}$ of the HFC338 has the same behavior as seen in Figure 2. The initial slope, at the high-temperature end of this curve could be approximated from the ratio of the vapor pressures of the components (letting the activity coefficient be unity); however, the necessary vapor pressure data would not normally be available in the case of an unidentified impurity. The curve shown for this $K_2^{\infty}$ in Figure 3 was calculated from,

$$\ln K_2^{\infty} = ag + bg^3 \qquad \textbf{(12)}$$

where *a* and *b* are fitted parameters and

$$g = (T_c/T)\tau^{\beta} \qquad \textbf{(13)}$$

At the other end of the bubble curve, the $K_1^{\infty}$ of the HFC245ca in Figure 3 follows eq.(11) because it is far removed from the azeotropic composition.

The above examples are useful for displaying the types of behavior $K_2^{\infty}$ can have when the identity of the impurity is known. Ebulliometry provides an accurate method for determining the value of the distribution coefficient at infinite dilution. The following example provides an illustration of the more typical problem with an impurity of unknown identity. Figure 4 shows the behavior of four impurities found in a sample of 1,1,1,3,3,3-hexafluoropropane (HFC236fa). These values of $K_2^{\infty}$ were found with eq.(6) from measurements made in a gas chromatograph using a column packed with Carbopac + 5% Fluorocol, and having a thermal conductivity detector. Analyses were made with the sample at 273 K, 297 K, and 338 K. After analysis of the sample that had been stored at ambient temperature, the sample was cooled in an ice bath for 18

hours, with occasional shaking to promote thermodynamic equilibrium. Samples from the liquid and vapor phases were analyzed and then the sample was heated for a similar length of time in a simple oven. Heating a low pressure container requires a certain amount of caution, and a careful estimation of the position of the liquid-vapor interface is necessary to avoid overpressuring the container. After allowance is made for the usual experimental uncertainties in chromatograms, it is seen that all impurities obey eq.(11), and the experimental vapor pressures could be easily corrected. The actual correction would depend upon the values of the liquid-phase mole fractions of the four impurities.

The final example illustrates a situation which is too often overlooked in experimental work. A sample of n-heptane was analysed with a gas chromatograph for impurities, and the above procedures were used make corrections to the measured vapor pressures. In this case, measurements were made on two sample loadings. When the first sample was removed from the apparatus, it was analysed again. Two additional very small peaks were found, and their position indicated impurities of high relative volatility. These two impurities were obviously volatile contaminants which originated in the sample cell. Their identities could be inferred from a knowledge of the previous contents of the sample cell. In this case they were the fluorinated propane and butane used in the study shown in Figure 3 above. This contamination occurred even though the apparatus had been evacuated and flushed with heptane several times.

Although we were unable in this instance to measure the $K_2^\infty$ of the contaminants with the chromatograph, their vapor pressures were known from the previous study, and we could use eq.(2) to estimate $K_2^\infty$ from the ratio of the vapor pressures. We assigned the value unity to the activity coefficient in eq.(2). Since the contaminents had similar vapor pressures, and since their combined mole fraction was very small, $z_2 \approx 2.5 \bullet 10^{-4}$, we treated them as a single impurity. Their $K_2^\infty$ was estimated to be about 15 at ambient temperature in the n-heptane.

The second sample was also analysed upon withdrawal from the apparatus, and it showed no spurious extra peaks. Apparently, the cell had been completely purged by the first sample. The results are shown in Figure 5 where it is seen that the contaminants had a significant impact on the measured vapor pressures of the first sample, even though they were very dilute. It is also seen that this correction technique, although it was very approximate, reconciled both sets of data to within their precision.

## Conclusions

We have combined several thermodynamic relationships with simple measurements to provide a method for correcting measured vapor pressures to account for the presence of impurities. We have verified that the temperature variation of the distribution coefficient, $K_2^{\infty}$ given by eq.(11), is valid down to a reduced temperature of at least 0.67, and it should be useable at even lower temperatures. However, if the impurity forms an azeotrope with the sample, then eqs.(10) and (11) are not complete as written and require an additional term. In that case, chromatograms must be measured at two or more temperatures. The water ice-point temperature provides a convenient additional datum. However, the chromatograms must be measured at temperatures at which the sample has an appreciable vapor pressure.

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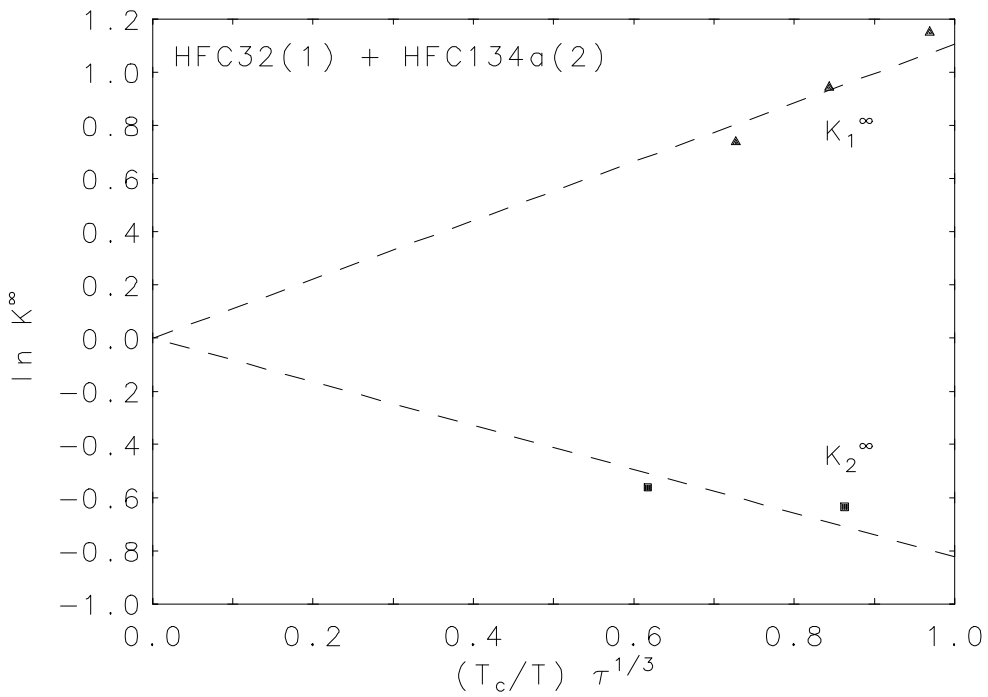


Figure 1. Distribution coefficient at infinite dilution for the mixture HFC32(1) + HFC134a(2); dashed lines are best fits of eq.(11); data from Weber and Silva (1996).

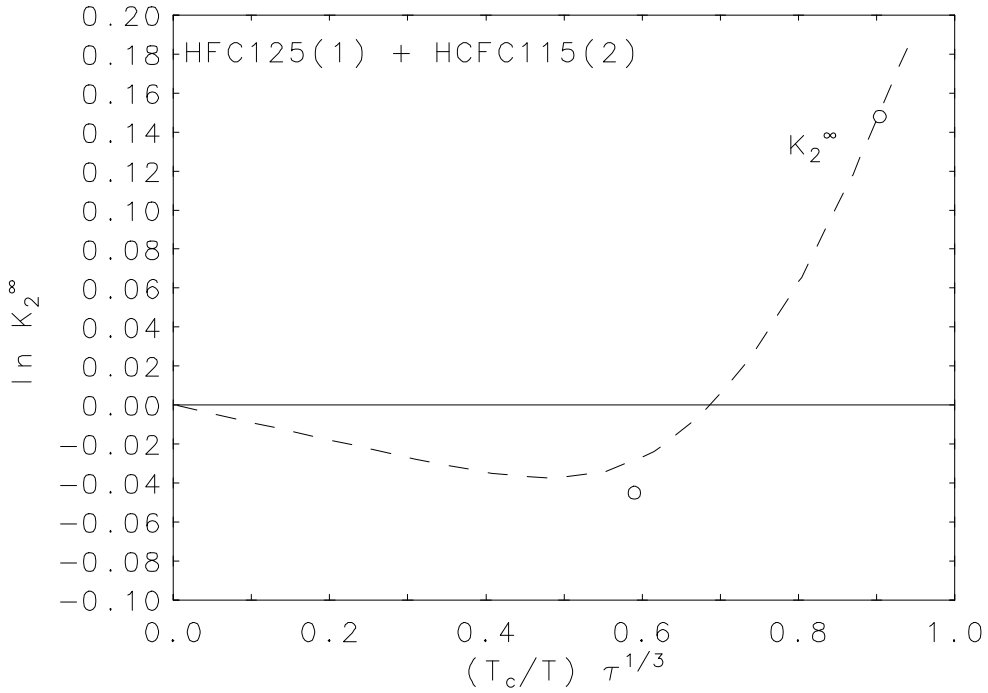


Figure 2. Infinite dilution K factor for HCFC115 in HFC125, showing the effect of azeotropic behavior; dashed curve is eq.(11) modified with a second term; data from Weber and Silva (1994).

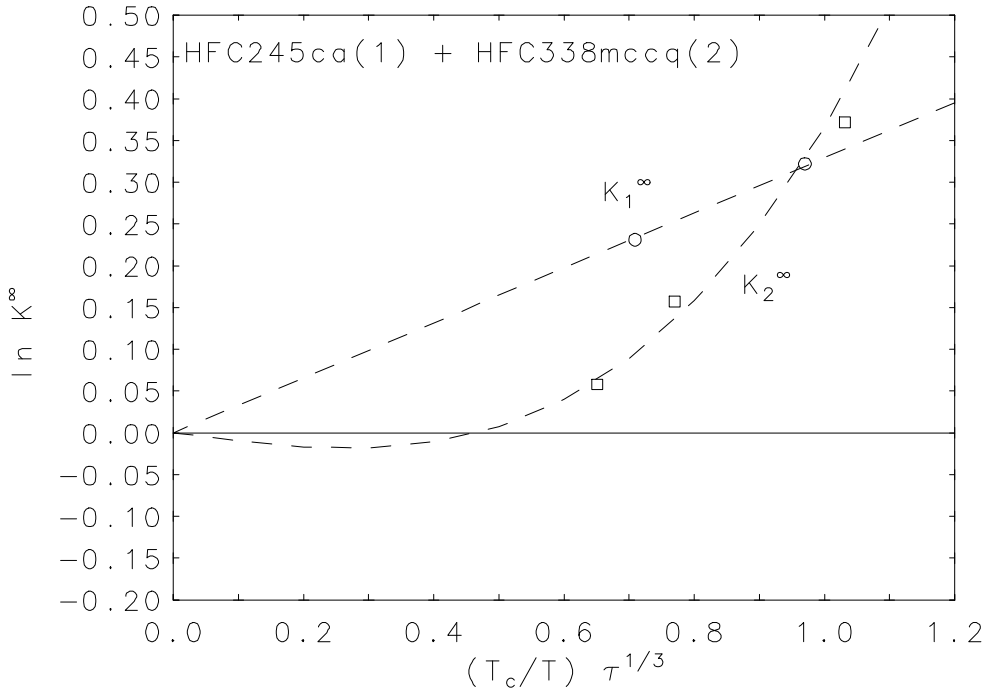


Figure 3. Infinite dilution K factors for the system HFC245ca + HFC338mccq. Azeotrope is seen to disappear at about 0.48; other end of the dew/bubble curve $(K_1^\infty)$ behaves normally and is represented by eq.(11); data from Weber and Defibaugh (1997).

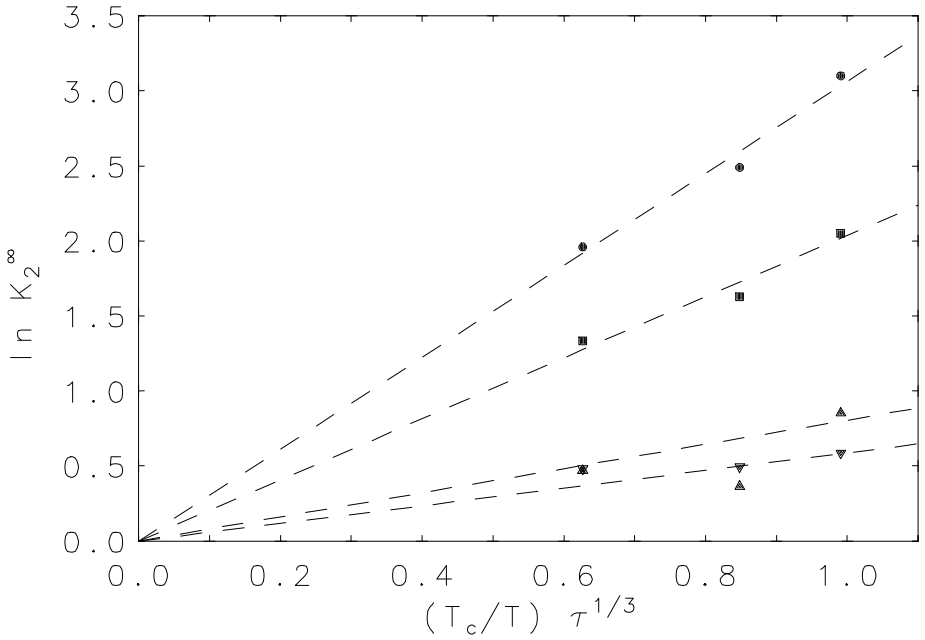


Figure 4. Temperature dependence of K factors for four unidentified impurities (designated by different symbols) in a sample of HFC236fa, measured with a gas chromatograph; dashed lines are best fits of eq.(11).

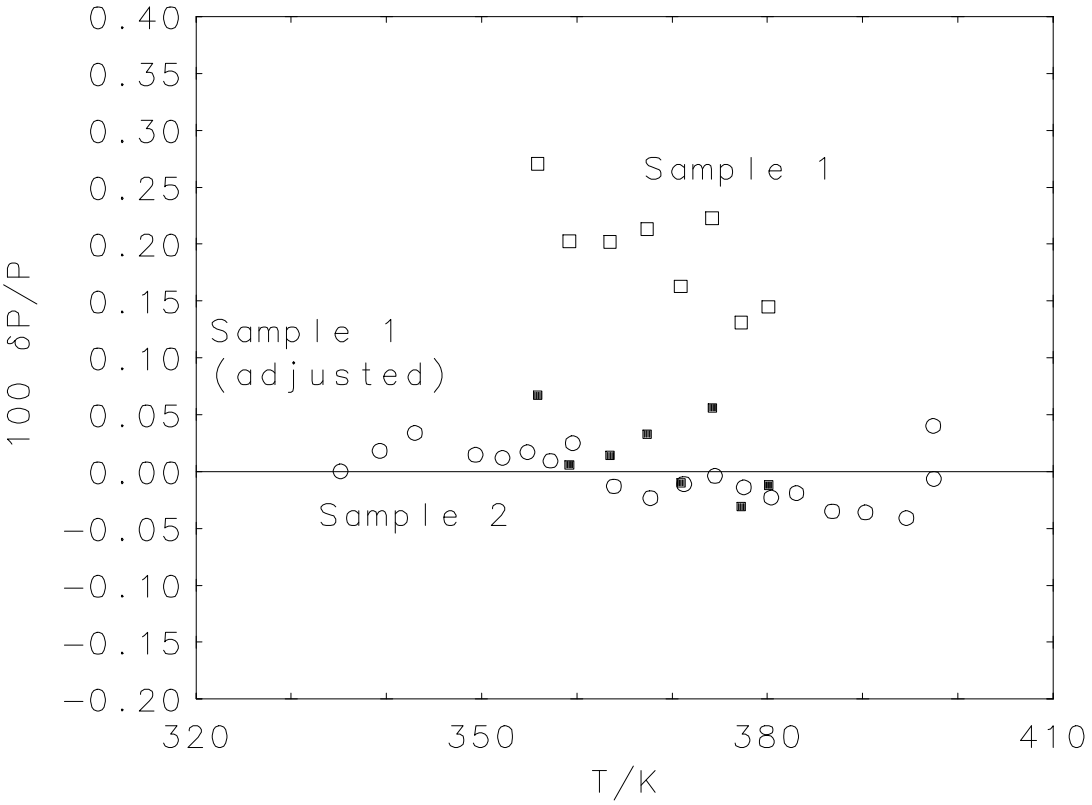


Figure 5. Effect of a very small volatile contaminant in □ sample 1 of n-heptane, $z_2 \approx 2.5 \bullet 10^{-4}$; ■ sample 1 data adjusted with eq.(3), ○ sample 2, not contaminated.