

1988

# Comparison of Equations of State for Application to Nonazeotropic Refrigerant Mixtures

K. D. Gerdsmeyer  
*University of Hannover*

H. Kruse  
*University of Hannover*

Follow this and additional works at: <http://docs.lib.purdue.edu/iracc>

---

Gerdsmeyer, K. D. and Kruse, H., "Comparison of Equations of State for Application to Nonazeotropic Refrigerant Mixtures" (1988). *International Refrigeration and Air Conditioning Conference*. Paper 37. <http://docs.lib.purdue.edu/iracc/37>

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact [epubs@purdue.edu](mailto:epubs@purdue.edu) for additional information.

Complete proceedings may be acquired in print and on CD-ROM directly from the Ray W. Herrick Laboratories at <https://engineering.purdue.edu/Herrick/Events/orderlit.html>

# COMPARISON OF EQUATIONS OF STATE FOR APPLICATION

## TO NONAZEOTROPIC REFRIGERANT MIXTURES

K. D. Gerdsmeier  
H. Kruse

University of Hannover  
Department of Refrigeration  
Welfengarten 1A, 3000 Hannover 1  
FEDERAL REPUBLIC OF GERMANY

### Abstract

The growing interest in recent years on nonazeotropic mixtures as working fluids for refrigeration systems and the necessity of calculating their thermodynamic behavior by the means of suitable equations of state for system simulation, designing refrigerant equipment etc., was the reason for a detailed comparison of three equations of state, i.e. the Lee-Kessler-Plocker equation, the Carnahan-Starling-DeSantis equation and the Redlich-Kwong-Soave equation, which have been applied to nonazeotropic mixtures in most of the current publications.

The purpose of this work was to discuss the behavior of these equations of state in predicting thermodynamic properties of nonazeotropic mixtures with particular regard to mixing rules, the adaptation of interaction parameters and to their accuracy depending on the variables of state, i.e. temperature, pressure, density and the composition. Measured data of vapor  $p$ ,  $v$ ,  $t$ ,  $x$ -properties, VLE behavior and liquid densities of several mixtures have been used to evaluate the comparison.

COMPARAISON DES EQUATIONS D'ETAT POUR L'APPLICATION AUX MELANGES DE FRIGORIGENES NON AZEOTROPIQUES.

RESUME : L'intérêt croissant, au cours des dernières années, pour les mélanges non azéotropiques en tant que frigorigènes et la nécessité de calculer leur comportement thermodynamique à l'aide d'équations d'état appropriées pour simuler les systèmes, concevoir les matériels frigorifiques, etc, a conduit à comparer de façon détaillée trois équations d'état : l'équation de Lee-Kessler-Plocker, l'équation de Carnahan-Starling-DeSantis et l'équation de Redlich-Kwong-Soave, qui ont été appliquées aux mélanges non azéotropiques dans la plupart des publications récentes.

L'objectif de cette étude était l'examen du comportement de ces équations d'état pour la prévision des propriétés thermodynamiques des mélanges non azéotropiques particulièrement du point de vue des règles de mélange, de l'adaptation des paramètres d'interaction et de leur précision suivant les variables d'état, à savoir la température, la pression, la masse volumique et la composition. Les valeurs mesurées des propriétés de la vapeur,  $p$ ,  $v$ ,  $t$ ,  $x$ , du comportement d'équilibre vapeur-liquide et des masses volumiques du liquide de plusieurs mélanges ont été utilisées pour évaluer la comparaison.

COMPARISON OF EQUATIONS OF STATE FOR APPLICATION  
TO NONAZEOTROPIC REFRIGERANT MIXTURES

K.D. Gerdsmeier H. Kruse

University of Hanover, Welfengarten 1 A  
D - 3000 Hanover 1

ABSTRACT

The growing interest in recent years on nonazeotropic mixtures as working fluids for refrigeration systems and the necessity of calculating their thermodynamic behavior by the means of suitable equations of state for system simulation, designing refrigerant equipment etc., was the reason for a detailed comparison of three equations of state, i.e. the Lee-Kesler-Plöcker equation, the Carnahan-Starling-DeSantis equation and the Redlich-Kwong-Soave equation, which have been applied to nonazeotropic mixtures in most of the current publications.

The purpose of this work was to discuss the behavior of these equations of state in predicting thermodynamic properties of nonazeotropic mixtures with particular regard to mixing rules, the adaptation of interaction parameters and to their accuracy depending on the variables of state, i.e. temperature, pressure, volume, and the composition. Measured data of vapor  $p, v, t, x$ -properties, VLE behavior and liquid volumes of the R22/R114 mixture have been used to evaluate the comparison.

NOMENCLATURE

a parameter of EOS  
b parameter of EOS  
k interaction parameter  
n number of data points  
p pressure  
T temperature (K)  
t temperature ( $^{\circ}\text{C}$ )  
v molar or specific volume  
x liquid concentration  
(mole fraction)  
y vapor concentration  
(mole fraction)

$\bar{\sigma}$  mean deviation  
 $\epsilon$  error function

Indices

cal calculated  
exp experimental  
i, j components of mixture  
m mixture  
r reduced

INTRODUCTION

Suitable equations of state for calculating thermodynamic properties of nonazeotropic refrigerant mixtures must be applied when such mixtures shall be used as working fluids for refrigerant systems. An estimation of the reliability of thermodynamic data calculated with those equations shall be carried out in this paper for three of the most used equations of state in current publications i.e. the Carnahan-Starling-DeSantis equation (CSD) /1/, the Lee-Kesler-Plöcker equation (LKP) /2/, and the Redlich-Kwong-Soave equation (RKS) /3/. Data of thermophysical variables of state calculated with these equations will be compared with measurements of vapor  $p, v, t, x$ -properties /4,5/, VLE /4/, and liquid densities /6/ of the R22/R114 mixture.

EQUATIONS OF STATE

A detailed description of the equations of state considered in this paper may be taken from references /1/, /2/, and /3/. Only some characteristic properties of them shall be pointed out here. The LKP equation is based on the method of corresponding states using a modified BWR-equation with generalized parameters. For pure substances only the critical values of temperature and pressure and the acentric factor must be known. Both of the other two equations (CSD, RKS) are two-parameter equations of the van-der-Waals type. They require adaptations of coefficients (two for RKS; six for CSD) for pure components, which have been described by Küver /7/ for

the refrigerants 22 and 114 and others. The CSD equation is expected to be of particular interest when predictions of liquid densities with high accuracy are necessary. An essential quality of the RKS equation is its fast computation. For all of the three equations of state mixing rules with one interaction parameter  $k_{ij}$  were proposed for the application to binaries.

#### DISCUSSION OF THE EQUATIONS OF STATE AT DIFFERENT SCOPES

The different characteristics of the three equations of state for estimating liquid volumes,  $p, t, x$ -behavior at vapor-liquid-equilibria and vapor properties will be emphasized by a comparison with measured values of the R22/R114 mixture. If nothing else will be mentioned, the interaction parameters applied in this section of the paper have been adapted only to VLE data /4/ by minimizing the mean deviation between calculated and measured pressures (equation (1)).

#### Liquid Volumes

The RKS equation will not be considered here in detail because of its well known fault in predicting liquid volumes. Its mean deviation from the liquid volumes measured by Valtz et al. /6/ amounts to more than 12%. The expected high accuracy of the CSD equation could be proved for the pure components (fig. 1) by deviations less than 1%, whereas for mixtures there is a remarkable influence of the interaction parameter. When optimizing the  $k_{ij}$  for this purpose, liquid volumes of mixtures will also be calculated with the same high accuracy, but the  $k_{ij}$  adapted to bubble pressures results in considerably stronger deviations, which even exceed 5% for other temperatures than plotted in fig. 1.

The volumes of both pure components calculated with the LKP equation differ from the measured values by less than 3% but with reversed sign. This is the reason why the influence of the  $k_{ij}$  is less important in this case and why the LKP equation enables an estimation of liquid volumes of the mixture with sufficient reliability, too. A similar behavior as plotted in fig. 1 was determined also for other temperatures.

#### Vapor liquid equilibria

First the three equations of state are compared in fig. 2 relating to bubble pressures of the pure components /4/. For both pure components, R22 and R114, the CSD and the RKS equation show similar behavior. For R22 the deviations from measured bubble pressures are lower than the values calculated with the LKP equation which are however lower than 0.8%. For R114 the deviations are all in all insignificantly higher.

With the CSD and RKS equation calculations of bubble pressures for mixtures result in considerably higher deviations from measured values /4/ as shown in fig. 3a for concentrations of about 0.5% R22 by mole. The corresponding results with the LKP equation are generally closer to the measured values with deviations comparable to those of the pure substances. The reproduction of the vapor composition for the same measured data points (fig. 3b) is better than 0.9% for the CSD and RKS equation and even better than 0.5% for the LKP equation.

The relationship between the concentration of the mixture and the reproduction of VLE data will be dealt with in a later section.

#### Vapor properties

In fig. 4 the behavior of the equations of state concerning vapor properties is illustrated by plotting the pressure deviation versus temperature for mixtures of 66.4% R22 by mole (50% by mass) and isochorics of 50 dm<sup>3</sup>/kg (measured data in /4/), 10 dm<sup>3</sup>/kg (/4/), and 2.55 dm<sup>3</sup>/kg (/5/). Very high accuracies in the whole plotted temperature ranges and quite similar behaviors can be observed at the two higher volumes for the CSD and the LKP equation whereas the RKS equation shows slightly stronger deviations. At the smaller volume of 2.55 dm<sup>3</sup>/kg, which is already close to the critical volume, the deviation increases for the LKP equation up to 2% and it

increases even more distinctly for the RKS equation up to about 8% as well as the influence of the temperature increases. The influence of the concentration is relatively small for all of the equations of state as fig. 5 shows for the volume of 50 dm<sup>3</sup>/kg.

#### ADAPTION OF INTERACTION PARAMETERS

The influence of the interaction parameters on the reliability of the calculated thermophysical data is shown exemplarily for the CSD equation in fig. 6, where mean deviations from all measured values of references /4/ and /6/ are plotted against  $k_{ij}$ . Obviously the interaction parameter has the strongest influence on the vapor-liquid-equilibria whereas the well reproduction of vapor properties is almost independent from  $k_{ij}$ . An interesting result is that the beneficial quality of the CSD equation in reproducing liquid volumes is most significant at an interaction parameter where the bubble pressures will be reproduced with a mean deviation of about 12%. If no measured data are available and thus an interaction parameter of  $k_{ij} = 0.0$  must be assumed the mean uncertainty of VLE calculations exceed 6% for the pressure, whereas the vapor property reproductions nearly reach the optimum.

With the exception of liquid volume estimations the behavior of the RKS equation is comparable to that of the CSD equation. The characteristic difference of the LKP equation consists in closer locations (referring to  $k_{ij}$ ) of the minimum values of the lines like plotted in fig. 6, in other words the smallest mean deviations of the considered values occur at less different interaction parameters.

The interaction parameters determined by the four most common methods of adaption, as described by equation (1) to (4) (where  $\epsilon_3$  represents the standard error), are also plotted in fig. 6 below the abscissa by marking the symbols of the four error functions.

$$\epsilon_1 = \frac{1}{n} \sum_i \left| \frac{P_{\text{col}} - P_{\text{exp}}}{P_{\text{exp}}} \right| \longrightarrow \min \quad (1)$$

$$\epsilon_2 = \frac{1}{n} \sum_i \left( \frac{P_{\text{col}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 \longrightarrow \min \quad (2)$$

$$\epsilon_3 = \sqrt{\frac{1}{n} \sum_i \left( \epsilon_1 - \frac{P_{\text{col}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2} \longrightarrow \min \quad (3)$$

$$\epsilon_4 = \frac{1}{n} \sum_i \left( \left( \frac{P_{\text{col}} - P_{\text{exp}}}{P_{\text{exp}}} \right)^2 + (y_{\text{col}} - y_{\text{exp}})^2 \right) \longrightarrow \min \quad (4)$$

In this case the adaptations according to  $\epsilon_1$  seems to be the best compromise, because all the other error functions, although decreasing the mean deviation for the vapor concentration  $y$ , considerably increase the mean deviations for the bubble pressures and for the liquid volumes. On the other hand the value of  $k_{ij}$  according to  $\epsilon_1$  yields to a mean deviation for  $y$  which is as half as big as the deviations for the bubble pressure and the liquid volume.

Therefore the mean deviations of the values considered in fig. 6 are summarized in fig. 7 for all three equations of state and for each of them by applying eq. (1) to determine the interaction parameter. It shall be pointed out that the LKP equation shows all at all the best reproduction of the measured values with mean deviations reaching not even 1.5% in all cases. The CSD equation yields to slightly better results for the vapor properties but for liquid densities only by the application of a different interaction parameter. Its mean deviation for the bubble pressures is relatively high, also in comparison with the RKS equation, which is except the liquid volume estimations moderately suitable taking into consideration its fast computations.

## MIXING RULES

Finally the influence of the mixing rules on the reproduction of VLE measurements /4/ shall be discussed. As for the LKP equation Plöcker's investigations /2/ concerned especially the optimization of the mixing rules, this equation will not be considered here for the moment. For the two other equations, CSM and RKS the same mixing rules (equations (5) to (7)) have been applied to the two parameters,  $a$  and  $b$  (see appendix). Therefore different mixing rules have been tested for the CSD equa-

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$a_{ij} = (1 - k_{ij}) (a_i a_j)^{1/2} \quad (6)$$

$$b_m = \sum_i \sum_j x_i x_j \frac{(b_i + b_j)}{2} \quad (7)$$

tion only and the results are plotted in fig. 8 related to the reproduction of vapor concentrations and in fig. 9 related to the reproduction of bubble pressures, where mixing rules A represent eq. (8) instead of eq. (6) and mixing rules B represent eq. (9) instead of eq. (7).

$$a_{ij} = (1 - k_{ij}) \frac{a_i + a_j}{2} \quad (8)$$

$$b_m = \sum_i x_i b_i \quad (9)$$

The differences in the results obtained by these three mixing rules are insignificant for both, deviations of vapor concentrations and bubble pressures, but for all of them a systematic dependency of the deviations from the liquid concentration can be observed. Applying the original mixing rules the  $k_{ij}$  has therefore been described as a function of liquid concentration by a second-order polynomial, which results in distinctly better reproduction of the measured data. As illustrated in fig. 10 also for the two other equations, RKS and LKP, the quality of reproduction of the measured data can be increased by applying such a concentration depending function for the interaction parameter.

In this context two particularities of the LKP equation compared with the other ones shall be mentioned: The mixing rules are not concerning the parameters of the equation of state, but the pseudocritical values which is characteristic for corresponding state methods, and the interaction parameter is fit to the pseudocritical temperature. Second, with the original mixing rules /2/ the influence of the concentration (fig. 8 and fig. 9) is less significant than for the CSD and the RKS equation and the reproduction of vapor concentrations is significantly better than shown in fig. 8 for the CSD equation.

## CONCLUSION

A comparison of three equations of state, CSD, LKP und RKS referred to measured data of the R22/R114 system has shown that the best reliability for calculations of liquid volumes, VLE-data, and vapor properties, will be reached all at all with the LKP equation. Much better results for liquid densities are possible with the CSD equation by using an interaction parameter optimized for that case. For many technical applications the reliability of the RKS equation, which runs 3 to 4 times faster than the other ones, is sufficient, too.

APPENDIX

RKS - equation: 
$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}$$

CSD - equation: 
$$p = \frac{RT(1+y+y^2-y^3)}{v(1-y)^3} - \frac{a}{v(v+b)}$$
 with  $y = b/4v$

REFERENCES

- /1/ Morrison, G.  
ASHRAE Trans., 1985, V. 91, Pt.1, pp 260-273
- /2/ Plöcker, U.  
Ph. D. thesis, 1977, TU Berlin
- /3/ Soave, G.  
Chem. Eng. Sci., Vol. 35, 1980, pp 1725-1729
- /4/ Kruse, H.; Gerdsmeier, K.D; Küver, M.  
Int. J. Refrig.; to be published in 1988
- /5/ Hasegawa, N.; Dematsu, M.; Watanabe, K.  
J. Chem. Eng. Data, 1985, 30, pp 32-36
- /6/ Valtz, A.; Laugier, S.; Richon, D.  
Int. J. Refrig.; 1986, Vol. 9, Sept., pp 282-289
- /7/ Küver, M.  
Research-report Nr. 20 of the DKV, 1987

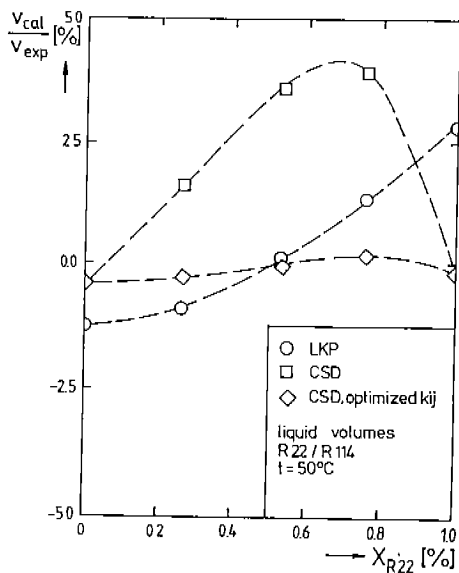


Figure 1

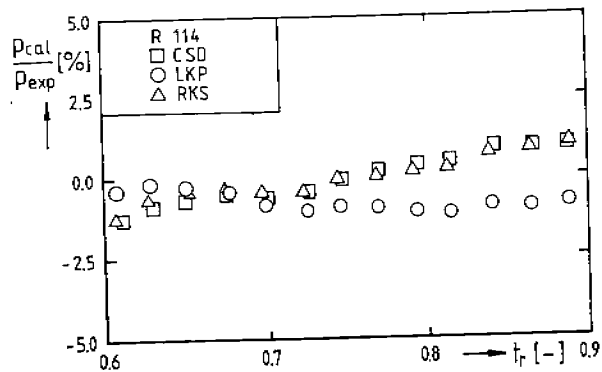
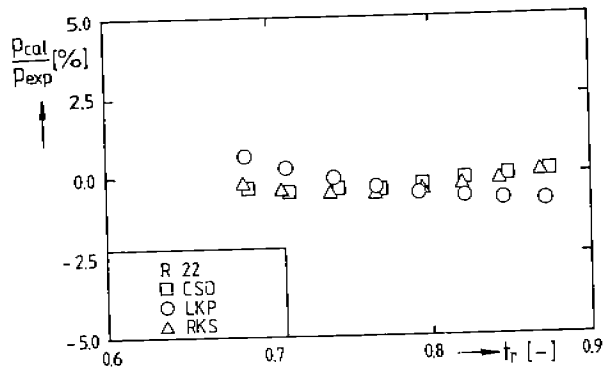


Figure 2

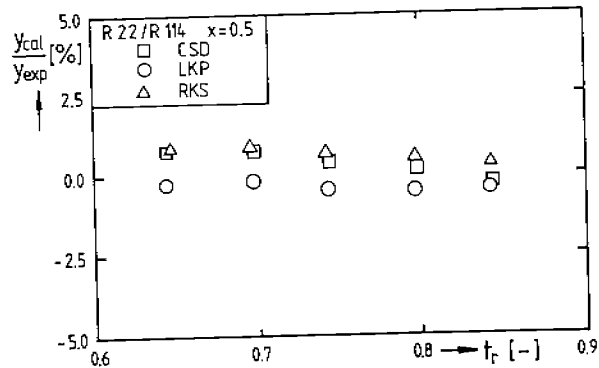
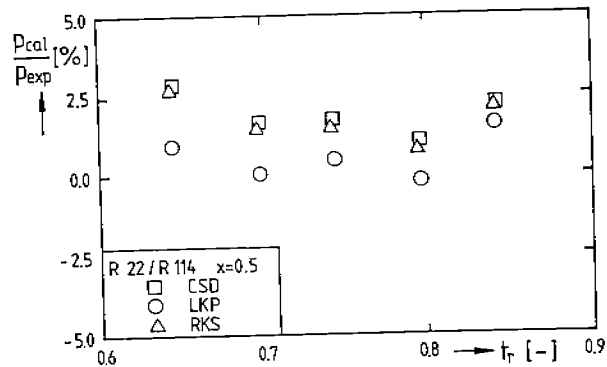


Figure 3



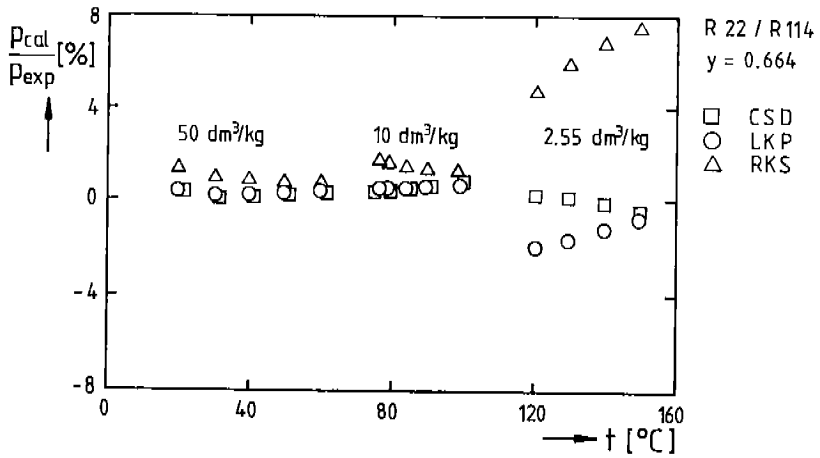


Figure 4

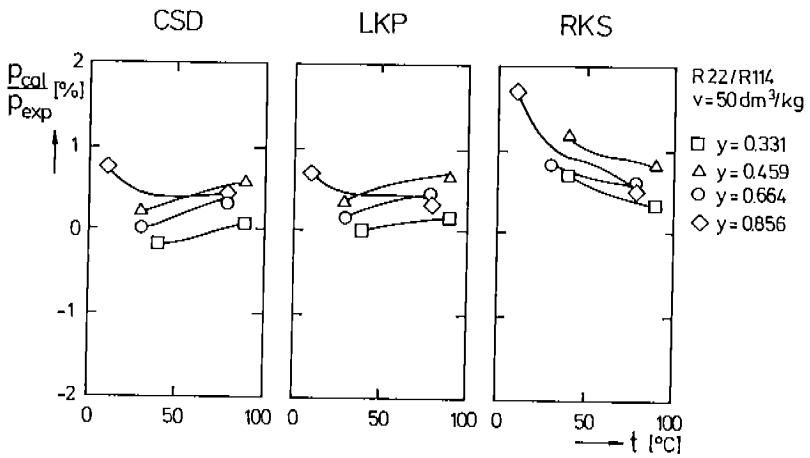


Figure 5

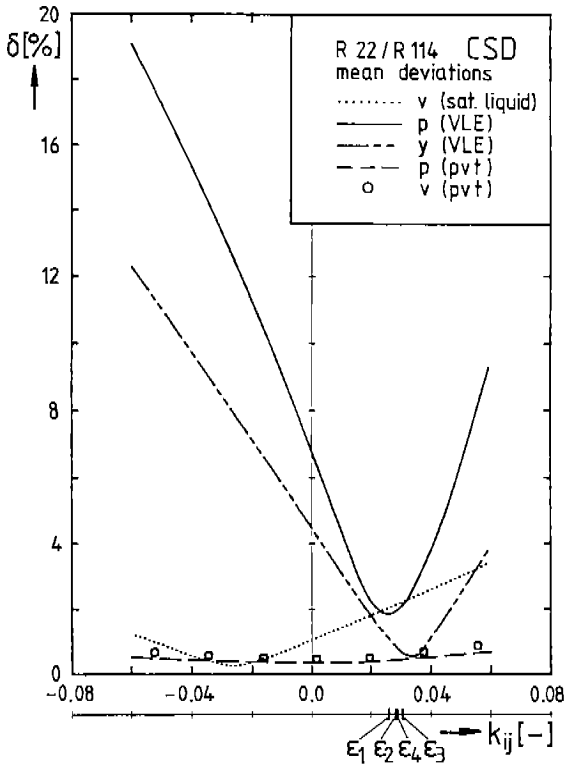


Figure 6

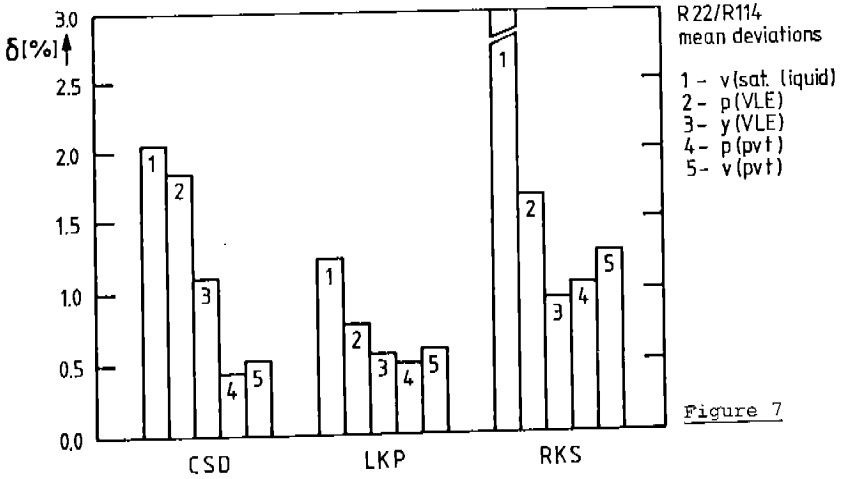


Figure 7

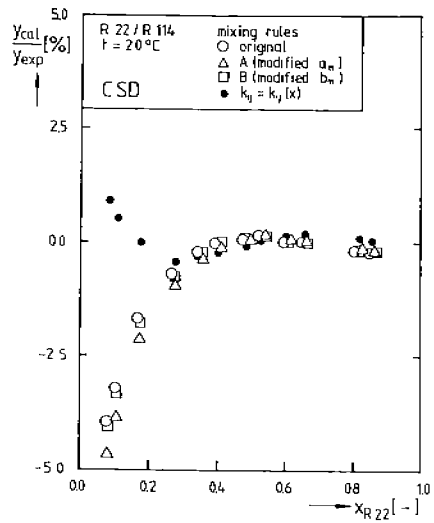


Figure 8

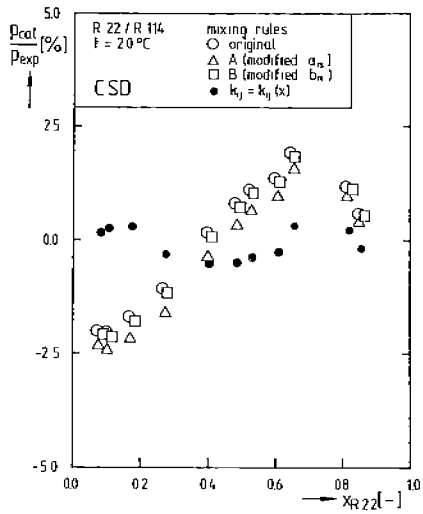


Figure 9

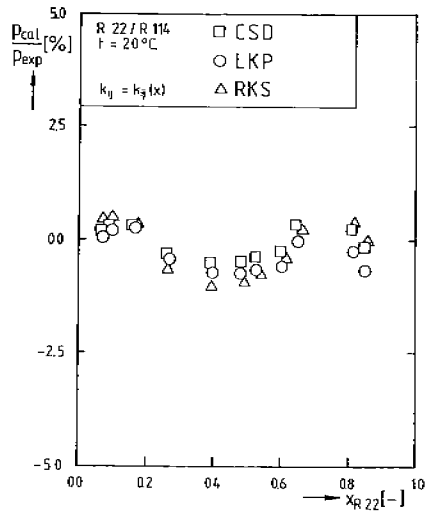


Figure 10