

# Vapor-Liquid Equilibrium in Binary Systems of *n*-Pentane + Chlorodifluoromethane or + 1,1,-Difluoroethane

Eva Fransson,<sup>†</sup> Alain Barreau, and Jean Vidal\*

Institut Français du Pétrole, 1-4 Avenue de Bois-Préau, Rueil-Malmaison, France

A constant-volume cell was used to determine vapor-liquid equilibria by the static method for the binary systems *n*-pentane + chlorodifluoromethane (R22) or + 1,1,-difluoroethane (R152a). Measurements were carried out between 303 and 383 K and between 0.3 and 4.4 MPa for different compositions of the mixtures. From the knowledge of the overall composition, the pressure, and the temperature, vapor and liquid compositions were calculated using the Soave-Redlich-Kwong equation of state together with an interaction parameter.

## Introduction

Mixtures of chlorofluoroalkanes have been of interest for some time as working fluids in heat pumps and refrigeration systems. As the restriction of the use of these compounds becomes more and more severe, hydrocarbons might be interesting alternatives. If the flammable hydrocarbons are mixed with nonflammable substances, the mixture compositions can be chosen to give nonflammable mixtures. In order to estimate the interaction parameters of equations of state for these systems, we need phase equilibrium data.

Very few data on systems of chlorofluorocarbons (CFC) with hydrocarbons have been published so far. We have chosen to make our measurements on two halogenated alkanes that are of high interest today when many CFCs are to be outphased by the Montreal protocol.

This paper presents a detailed explanation of the experimental method, the experimental data, a short section about the exploitation of the data, and the interaction parameters calculated for the two mixtures.

## Experimental Section

**Apparatus.** The equipment is represented in Figure 1. It consists of three different parts: the cell and the measurement unit, the thermostatic bath, and the filling equipment.

**1. The Cell and the Measurement Unit.** The cell (A) has been realized in the laboratory workshop. It can be dismantled into three different pieces, and the contact surfaces are silver plated to ensure a perfect hermetic contact between the different pieces. For a temperature between 253 and 473 K, the cell has the following mechanical limits; operating pressure 7 MPa, test pressure 13 MPa. The weight of the empty cell is 950 g. Through an isolation valve (M), the cell is connected to the measurement unit (C). This unit consists of a pressure transducer (CEC-1004), a platinum resistance thermometer (Thermo-Est, 100  $\Omega$ ), a safety rupture valve, and a connection valve (D) that isolates the cell and the measurement unit from the filling equipment during the measurements. The pressure transducer is isolated from the fluid of the thermostatic bath by a bell-shaped steel protection. The absolute pressure is registered by a membrane which is in contact with the vapor phase. The transducer is supplied with 10 V, and its maximum output signal is 30 mV. The instrument is compensated in temperature between 300 and 473 K, and its precision is 0.25%. The calibration was made using a dead weight gauge (Desgranges et Huot) at four tem-

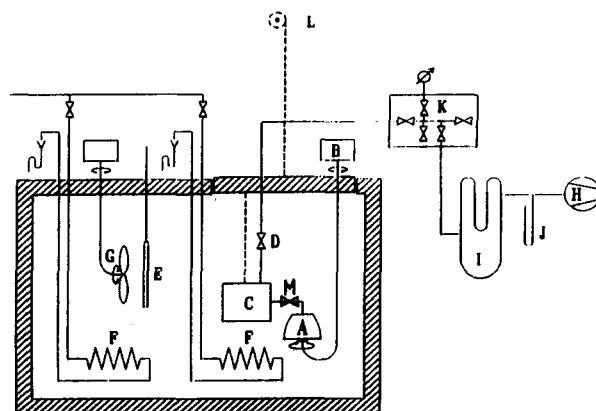


Figure 1. Sketch of the experimental apparatus for measuring vapor-liquid equilibria: A, cell; B, magnetic stirrer; C, measurement unit; D, valve; E, electric resistance; F, refrigeration coil; G, propeller stirrer; H, vacuum pump; I, vacuum trap; J, gauge; K, group of valves; L, crank; M, isolation valve.

Table I. Vapor Pressures  $P$  of Pure Components at Temperature  $T$ : Experimental (Exptl) and Literature (Lit.) Values Obtained by Interpolation from the Data Given in Reference 1 and Percentage Relative Deviation  $\Delta P/P$

product	$T_{\text{exptl}}/K$	$P_{\text{exptl}}/MPa$	$P_{\text{lit.}}/MPa$	$(\Delta P/P)/\%$
<i>n</i> -pentane	323.70	0.166	0.163	2.15
	343.89	0.293	0.288	1.63
	364.05	0.481	0.480	0.30
	384.54	0.754	0.762	1.
R22	303.78	1.227	1.212	1.2
	323.62	1.975	1.965	0.51
	303.87	0.711	0.701	1.37
R152a	323.73	1.203	1.196	0.29
	343.94	1.932	1.943	0.57
	364.08	2.944	2.979	1.19
	384.58	4.375	4.397	0.50

peratures  $T$ , 298, 323, 343, and 363 K, and 17 different pressure  $P$  levels. Ten coefficients were fitted to a third-degree polynomial, which is a function of the voltage and the temperature. The standard deviation in pressure is 1.8 kPa. The platinum resistance thermometer was calibrated using a reference thermometer (IPTS-68) in the same temperature range. A polynomial allows the fitting of the calibration data with a standard deviation in temperature of 0.005 K.

During the measurements, the connection valve (M) is opened and the mixture occupies the cell and the measurement unit. The total volume was determined to be  $60.44 \pm 0.05$  cm<sup>3</sup> by measurement of pressure and temperature for different fillings of nitrogen and using a high-precision equation of

\* To whom correspondence should be addressed.

<sup>†</sup> Present address: Department of Heat and Power Technology, Chalmers University of Technology, 412 96 Göteborg, Sweden.

**Table II. Gas-Liquid Critical Properties, Temperature  $T_c$  and Pressure  $P_c$ , Acentric Factor  $\omega$ , and Translation Parameters  $c$  for *n*-Pentane, R22, and R152a**

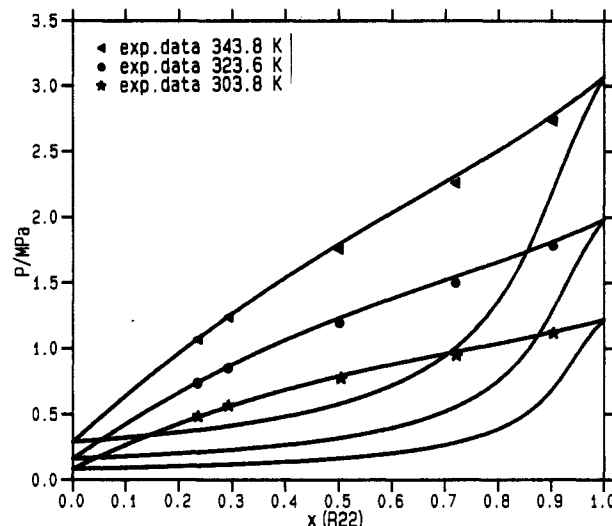
product	$T_c$ /K	$P_c$ /MPa	$\omega$	$c$ /(cm <sup>3</sup> mol <sup>-1</sup> )
<i>n</i> -pentane	469.74	3.37	0.251	10.97
R22	369.2	4.98	0.22	9.29
R152a	386.65	4.495	0.256	13.6

state. A magnetic stirrer (B) enables the mixture to rapidly reach the equilibrium.

**2. The Thermostatic Bath.** The thermostatic bath has a capacity of 70 L and contains a synthetic oil. The utilization range for the oil is 300–473 K. The energy is supplied by an electric resistance (E), and the regulation is improved by a cold water circulation (F). To assure a homogeneous temperature, a propeller stirrer is set in the bath. The temperature stability is 0.01 K.

**3. The Filling Equipment.** The filling equipment contains a vacuum pump (H) that is used to evacuate the air in the cell and to degass the liquid components. This pump is protected by a vacuum trap immersed in liquid nitrogen, and the vacuum (1 Pa) is registered by a gauge (J). The successive fillings and emptyings are carried out by means of a group of valves (K) coupled with a number of warming and freezing periods of the vessel.

**Procedure.** A thorough cleaning of the vessel is done every time a new binary mixture is to be introduced. Between each filling of the vessel with different compositions of the same binary system, several cleanings with acetone or another solvent are performed. This is done without dismantling the cell and is repeated until the initial weight of the empty unit is recovered. The composition of the mixture is determined by successive weighings during the filling procedure with a precision balance (0.1 mg). The cell is connected to the filling equipment through valve D and evacuated with the vacuum pump. Then valves D and M are closed, and the cell is weighed. The quantity of each component is estimated, from an approximate knowledge of its density, in order to fill the vessel with a liquid phase of about  $2/3$  of its volume. After



**Figure 2.** Vapor-liquid equilibrium pressure for the R22 (1) + *n*-pentane (2) system: lines, calculated with the Soave method; points, experimental data, as a function of the mole fraction of component 1.

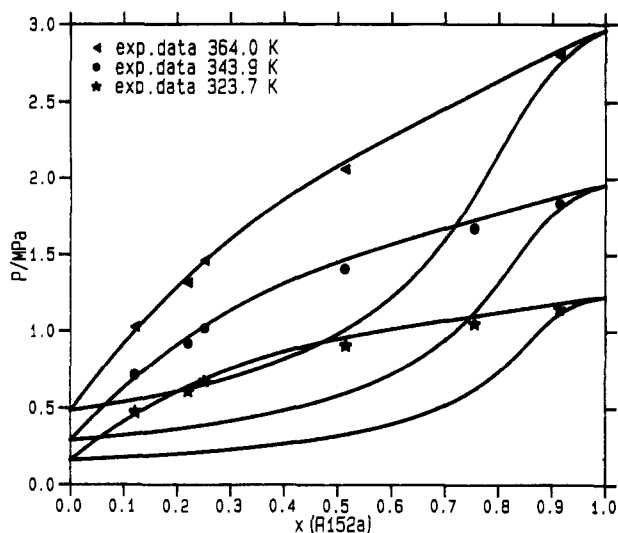
each introduction, the cell is again weighed. The introduction procedure depends on the state of the constituent at ordinary temperature and pressure.

The liquid component is introduced by means of a graded buret connected to the cell through valve D. This introduction is gravity-fed and easily realized since the cell is initially at vacuum. Then the cell is immersed in dry ice and again connected through valve D to the vacuum equipment to be degassed.

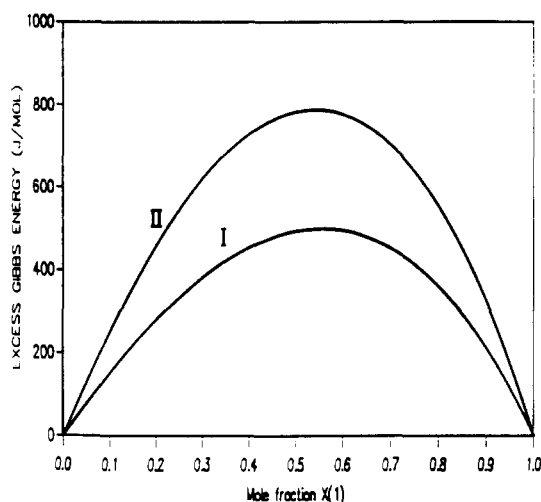
The gaseous component is introduced through valve D. The pressure of the gas must be considerably higher than the pressure of the vessel. This is necessary in order to avoid inverse diffusion. The vessel can be cooled and the gas container heated in order to obtain good transfer conditions. Finally, valve D is closed, and the cell is connected to the

**Table III. Experimental (Exptl) and Calculated (Calcd) Data for the R22 (1) + *n*-Pentane (2) System: Masses  $m_i$ , Overall Mole Fractions  $z_i$ , Temperature  $T$ , Pressure  $P$ , Liquid Mole Fractions  $x_i$ , Vapor Mole Fractions  $y_i$ , Relative Pressure Deviation  $\Delta P/P$ , and Optimal Interaction Parameter  $k_{ij}$** 

$m_1$ /g	$m_2$ /g	$z_1$	$T_{\text{exptl}}/K$	$P_{\text{exptl}}/\text{MPa}$	$P_{\text{calcd}}/\text{MPa}$	$x_1$	$y_1$	$(\Delta P/P)/\%$	$k_{ij}$
36.9074	3.1993	0.9059	304.03	1.125	1.125	0.9039	0.9771	-0.09	
27.3573	8.5986	0.7264	303.86	0.956	0.975	0.7219	0.9504	2.0	
17.4619	13.8427	0.5128	303.83	0.786	0.796	0.5042	0.9212	1.2	0.0925
17.4619	13.8427	0.5128	303.70	0.783	0.793	0.5042	0.9213	1.3	
11.5487	22.8083	0.2970	304.12	0.573	0.565	0.2929	0.8690	-1.3	
9.5041	22.3083	0.2413	303.82	0.493	0.484	0.2361	0.8435	-1.8	
36.9074	3.1993	0.9059	323.64	1.793	1.801	0.9033	0.9713	0.45	
27.3573	8.5986	0.7264	323.67	1.510	1.539	0.7194	0.9349	1.9	
17.4619	13.8427	0.5128	323.65	1.205	1.227	0.5016	0.8946	1.8	
11.5487	22.8083	0.2970	323.63	0.860	0.857	0.2924	0.8280	-0.37	0.0960
11.5487	22.8083	0.2970	323.59	0.860	0.856	0.2924	0.8281	-0.45	
8.5041	22.3083	0.2413	323.65	0.743	0.738	0.2351	0.7950	-0.65	
8.5041	22.3083	0.2413	323.57	0.749	0.737	0.2352	0.7952	-1.6	
36.9074	3.1993	0.9259	343.83	2.741	2.758	0.9033	0.9629	0.63	
27.3573	8.5986	0.7264	343.87	2.270	2.301	0.7186	0.9140	1.4	
17.4619	13.8427	0.5128	343.78	1.769	1.787	0.4998	0.8609	0.99	
17.4619	13.8427	0.5128	343.84	1.768	1.788	0.4998	0.8608	1.2	0.0936
11.5487	22.8083	0.2970	343.83	1.250	1.240	0.2928	0.7781	-0.82	
11.5487	22.8083	0.2970	343.80	1.250	1.239	0.2928	0.7781	-0.87	
8.5041	22.3083	0.2413	343.85	1.081	1.069	0.2349	0.7377	-1.1	
36.9074	3.1993	0.9059	363.98	3.998	4.031	0.9063	0.9477	0.84	
27.3573	8.5986	0.7264	364.01	3.241	3.282	0.7213	0.8836	1.3	
17.4619	13.8427	0.5128	363.95	2.477	2.502	0.5003	0.8185	1.0	
17.4619	13.8427	0.5128	363.97	2.472	2.503	0.5003	0.8185	1.2	0.0936
11.5487	22.8083	0.2970	363.98	1.765	1.738	0.2947	0.7230	-1.5	
8.5041	22.3083	0.2413	364.01	1.512	1.502	0.2357	0.6771	-0.64	
8.5041	22.3083	0.2413	363.94	1.518	1.501	0.2357	0.6771	-1.1	
17.4619	13.8427	0.5128	384.47	3.343	3.382	0.5062	0.7628	1.2	0.0952
8.5041	22.3083	0.2413	384.40	2.079	2.056	0.2385	0.6101	-1.1	



**Figure 3.** Vapor-liquid equilibrium pressure for the R152a (1) + *n*-pentane (2) system: lines, calculated with the Soave method, points, experimental data, as a function of the mole fraction of component 1.



**Figure 4.** Molar excess Gibbs energy  $G^E$  calculated with the Soave-Redlich-Kwong equation of state as a function of mole fraction of component 1: curve I, R22 (1) + *n*-pentane (2) at 324 K and 2 MPa; curve II, R152a (1) + *n*-pentane (2) at 324 K and 1.2 MPa.

measurement unit through valve M.

**Chemicals.** The chemicals that were used are *n*-pentane (pure, >99%) from Fluka AG, chlorodifluoromethane (R22), and 1,1-difluoroethane (R152a) from Dehon Service. The purity of the products and the reliability of our equipment were tested by comparison of our measurements (Table I) with literature data (1).

### Exploitation of the Experimental Data

The primary experimental data are the measured temperature  $T_{\text{exptl}}$  and pressure  $P_{\text{exptl}}$ , the total volume of the system  $V_{\text{tot}}$ , and the masses of each product,  $m_1$  and  $m_2$ , which give us the overall mole fraction  $z_i$ . The liquid  $x_i$  and vapor  $y_i$  mole fractions should be determined by analysis of both phases. However, a good approximation of these values can be obtained using an equation of state and applying it simultaneously to the whole set of experimental data. We used the Soave model (2), associated with the volume correction proposed by Peneloux and Rauzy (3), eqs 1-6, where  $v_{\text{calcd}}$  is calculated using eq 1,  $c$  is the translation parameter, and  $v_{\text{corr}}$  the corrected volume. For the pure components, the

$$P = \frac{RT}{v_{\text{calcd}} - b} - \frac{a}{v_{\text{calcd}}(v_{\text{calcd}} + b)} \quad (1)$$

$$a = \sum_i \sum_j a_{ij} z_i z_j \quad (2)$$

$$b = \sum_i b_i z_i \quad (3)$$

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \quad (4)$$

$$v_{\text{corr}} = v_{\text{calcd}} - c \quad (5)$$

$$c = \sum_i c_i z_i \quad (6)$$

parameters  $a_i$  and  $b_i$  of the Redlich-Kwong equation of state are obtained by applying relations 7-10, as proposed by Soave (2).

$$a = 0.42748 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (7)$$

$$\alpha(T) = (1 + \lambda (1 - (T/T_c)^{1/2}))^2 \quad (8)$$

$$\lambda = 0.48 + 1.574\omega - 0.176\omega^2 \quad (9)$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (10)$$

The values of the gas-liquid critical properties, temperature  $T_c$  and pressure  $P_c$ , of the acentric factors  $\omega$ , and of the translation parameters  $c$  are given in Table II. The values of the translation parameters have been determined from the density at the normal boiling point.

Starting from an initial value of the interaction parameter  $k_{ij}$ , eq 4, and for each experimental point from the data  $T_{\text{exptl}}$ ,  $V_{\text{tot}}$ ,  $m_1$ , and  $m_2$ , the equilibrium pressure  $P_{\text{calcd}}$  is calculated. This step involves the calculation of the vapor-liquid equilibria using the equation of state and the equilibrium conditions and gives us, together with  $P_{\text{calcd}}$ , the values of the quantities of vapor and liquid phases, their volumes, and their compositions. Then the mean quadratic relative deviation is calculated as

$$\sigma_P = \left( \frac{\sum \left( \frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}} \right)^2}{n} \right)^{1/2} \quad (11)$$

where  $n$  is the number of experimental points. The best value of the interaction parameter  $k_{ij}$  is obtained by minimizing  $\sigma_P$ . The phase compositions calculated in such a way depend on the quality of the model, and should not be accepted if the correlation of the pressures is bad. From the values in Tables III and IV it appears that the relative deviations

$$\frac{\Delta P}{P} = \frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}} \quad (12)$$

between the calculated and experimental values of the pressure are larger than the experimental uncertainty. However, taking into account the errors in temperature, mass of the components, total volume, and the simplicity of the model, the deviation is reasonable. Furthermore, due to the quantities introduced in the cell and to the relatively low pressure range, the differences between the liquid-phase compositions calculated in this way and the overall compositions determined from the mass of each component are small

**Table IV. Experimental (Exptl) and Calculated (Calcd) Data for the R152a (1) + *n*-Pentane (2) System: Masses  $m_i$ , Overall Mole Fractions  $z_i$ , Temperature  $T$ , Pressure  $P$ , Liquid Mole Fractions  $x_i$ , Vapor Mole Fractions  $y_i$ , Relative Pressure Deviation  $\Delta P/P$ , and Optimal Interaction Parameter  $k_{ij}$** 

$m_1/g$	$m_2/g$	$z_1$	$T_{\text{exptl}}/K$	$P_{\text{exptl}}/MPa$	$P_{\text{calcd}}/MPa$	$x_1$	$y_1$	$(\Delta P/P)/\%$	$k_{ij}$
31.6242	3.2242	0.9146	303.90	0.679	0.691	0.9142	0.9562	1.8	
27.2814	9.6235	0.7559	303.90	0.628	0.648	0.7549	0.9199	3.1	
27.2814	9.6235	0.7559	303.80	0.630	0.646	0.7549	0.9199	2.5	
13.5914	13.6248	0.5215	303.88	0.555	0.579	0.5162	0.8892	4.3	
13.5914	13.6248	0.5215	303.77	0.559	0.577	0.5162	0.8893	3.3	0.1376
7.1280	22.6816	0.2556	303.95	0.429	0.425	0.2519	0.8233	-0.96	
7.1280	22.6816	0.2556	303.79	0.431	0.423	0.2519	0.8236	-1.8	
5.7578	21.4305	0.2269	303.94	0.390	0.397	0.2221	0.8077	1.7	
3.0527	23.1280	0.1260	303.88	0.305	0.280	0.1224	0.7142	-8.1	
31.6242	3.2242	0.9146	323.77	1.151	1.164	0.9141	0.9515	1.1	
27.2814	9.6235	0.7559	323.72	1.054	1.081	0.7550	0.9059	2.6	
27.2814	9.6235	0.7559	323.65	1.057	1.079	0.7550	0.9060	2.1	
13.5914	13.6248	0.5215	323.73	0.910	0.947	0.5144	0.8630	4.	
13.5914	13.6248	0.5215	323.66	0.916	0.945	0.5144	0.8631	3.2	0.1448
7.1280	22.6816	0.2556	323.75	0.681	0.681	0.2511	0.7800	0.02	
7.1280	22.6816	0.2556	323.67	0.683	0.680	0.2511	0.7802	-0.43	
5.7578	21.4305	0.2269	323.77	0.615	0.635	0.2208	0.7608	3.3	
3.0527	23.1280	0.1260	323.74	0.476	0.454	0.1214	0.6524	-4.6	
3.0527	23.1280	0.1260	323.69	0.485	0.453	0.1214	0.6525	-6.5	
31.6242	3.2242	0.9146	343.96	1.844	1.854	0.9142	0.9476	0.52	
27.2814	9.6235	0.7559	343.91	1.685	1.701	0.7558	0.8905	0.96	
27.2814	9.6235	0.7559	343.91	1.677	1.701	0.7558	0.8905	1.4	
13.5914	13.6248	0.5215	343.93	1.411	1.448	0.5133	0.8312	2.6	
13.5914	13.6248	0.5215	343.89	1.418	1.447	0.5133	0.8313	2.0	
7.1280	22.6816	0.2556	343.94	1.025	1.020	0.2511	0.7278	-0.48	0.1472
7.1280	22.6816	0.2556	343.92	1.027	1.020	0.2511	0.7278	-0.72	
5.7578	21.4305	0.2269	343.97	0.924	0.950	0.2200	0.7045	2.8	
5.7578	21.4305	0.2269	343.90	0.929	0.949	0.2200	0.7047	2.1	
3.0527	23.1280	0.1260	343.94	0.721	0.688	0.1208	0.5822	-4.5	
3.0527	23.1280	0.1260	343.90	0.730	0.688	0.1208	0.5824	-5.8	
31.6242	3.2242	0.9146	364.12	2.808	2.807	0.9150	0.9425	-0.05	
13.5914	13.6248	0.5215	364.11	2.068	2.092	0.5139	0.7926	1.2	
7.1280	22.6816	0.2556	364.10	1.470	1.449	0.2523	0.6691	-1.5	0.1464
5.7578	21.4305	0.2269	364.13	1.323	1.349	0.2204	0.6421	1.9	
3.0527	23.1280	0.1260	364.07	1.035	0.994	0.1209	0.5101	-4.0	
13.5914	13.6248	0.5215	384.61	2.912	2.958	0.5198	0.7418	1.6	
7.1280	22.6816	0.2556	384.59	2.162	2.039	0.2558	0.6085	-5.7	0.1528
5.7578	21.4305	0.2269	384.64	1.829	1.899	0.2225	0.5793	3.8	
3.0527	23.1280	0.1260	384.61	1.449	1.425	0.1218	0.4453	-1.7	

and the calculation procedure is just a correction procedure for the overall composition.

## Results

All the experimental values, together with the calculated values of the pressure and of the phase compositions, are listed in Tables III and IV. The general behavior of the vapor-liquid equilibrium diagram is shown in Figures 2 and 3 (only three isotherms are shown for the sake of clarity). For each isotherm, the best value of the interaction parameter  $k_{ij}$  is given. It clearly appears that this parameter cannot be neglected, but as it can be seen, the variation with temperature is very low and the whole set of data can be correlated with a single value:

$$\text{R22} + n\text{-pentane} \quad k_{ij} = 0.0934 \quad \sigma_P = 0.013$$

$$\text{R152a} + n\text{-pentane} \quad k_{ij} = 0.141 \quad \sigma_P = 0.031$$

Using the Soave-Redlich-Kwong equation of state, it is possible to calculate the molar excess Gibbs energy of both systems; however, it should be underlined that the pressure must be fixed since the model takes into account the influence of this variable. The calculations have been done at 324 K, and at a pressure equal to the vapor pressure of the lightest component, so both components and the mixture are stable in the liquid state in the whole composition range. The results of this calculation are shown in Figure 4; considering the model which has been applied, they should be regarded as merely a semiquantitative estimation of  $G^E$ .

## Conclusions

The vapor-liquid equilibrium pressures for the R22 + *n*-pentane and R152a + *n*-pentane mixtures in the temperature range between 304 and 384 K can be correlated using the Soave method together with the classical mixing rules and an adjusted interaction parameter. The results may be used for engineering calculations. It is well known that the Soave-Redlich-Kwong method is usually applied to nonpolar systems, e.g., hydrocarbon mixtures. However, in the present case the polarity effect does not prevent a fair correlation of the data. The same method has already been applied to trifluoromethane +  $C_5$  hydrocarbon systems (4). Using the same equation of state, it is also possible to determine the thermodynamic properties (enthalpy, entropy) which are necessary for the calculation of refrigeration cycles.

## Glossary

$a, b$	Soave-Redlich-Kwong equation of state parameters
$c$	translation parameter
$k_{ij}$	interaction parameter
$m$	mass
$P$	pressure
$R$	molar gas constant
$T$	temperature
$v_{\text{calcd}}$	calculated molar volume
$v_{\text{corr}}$	corrected molar volume
$x$	liquid mole fraction
$y$	vapor mole fraction
$z$	overall mole fraction

$\lambda$  parameter in the  $\alpha(T)$  law  
 $\sigma_P$  mean relative quadratic deviation

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