A Recirculation Apparatus for Vapor-Liquid Equilibrium Measurements of Refrigerants. Binary Mixtures of R600a, R134a and R236fa

SERGIO BOBBO*

Istituto per la Tecnica del Freddo, Consiglio Nazionale delle Ricerche
Corso Stati Uniti, 4. I-35133 Padova PD Italy
E-mail: sergio@itef.pd.cnr.it
phone: [+39] (49) 8295736 fax: [+39] (49) 8295728

ROMAN STRYJEK

Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44/52. 01-224 Warsaw Poland

NICOLA ELVASSORE, ALBERTO BERTUCCO

Istituto di Impianti Chimici, Università di Padova
Via Marzolo, 9 I-35131 Padova PD Italy

* corresponding author

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Abstract

A set-up for the measurement of vapor-liquid equilibria (*p-T-x-y)* data on refrigerant systems was designed, built and tested. The recirculation method was used and the vapor phase was forced through the liquid one by a magnetic pump. The thermodynamic equilibrium was reached in a viewing cell with an inside volume of 50 cm^3. The composition of the phases were analyzed by a gas chromatograph connected on-line with either FID or TCD detectors. The operating temperature and pressure in the apparatus range from 240 to 400 K and from 0.1 to 10 MPa, respectively. The estimated accuracy of the measured data was 0.01 K for temperature, 0.5 kPa for pressure and 0.001 for liquid and vapor compositions. Vapor-liquid equilibria data were obtained for the following systems: 1,1,1,2-tetrafluorethane + isobutane (R134a + R600a) at 293.66 K and 303.68 K; 1,1,1,2-tetrafluorethane + 1,1,1,3,3,3-hexafluoropropane (R134a + R236fa) at 283.62 K and 303.68 K; isobutane + 1,1,1,3,3,3-hexafluoropropane (R600a + R236fa) at 303.68 K. The thermodynamic consistency of the experimental results was tested.

Introduction

As a result of the Montreal Protocol regulations and their implementation, chlorofluorocarbons (CFCs) have already been banned, and hydrochlorofluorocarbons (HCFCs) are also going to be phased out within the next twenty years. It is consequently necessary to seek alternatives with suitable thermodynamic properties. It is now evident that the substitute refrigerants are generally binary or ternary mixtures rather than pure compounds. Investigating the vapor-liquid equilibrium (VLE) behavior of these new-generation refrigerant mixtures is of paramount importance because the resulting information is essential both for checking the quality of the models and for designing or

retrofitting currently-operating refrigeration plants. The present work gives a detailed description of a new apparatus and a VLE measuring method oriented to refrigerant mixtures. It also reports the results of VLE measurements and thermodynamic consistency checks on the three binary systems derived from the ternary mixture 1,1,1,2-tetrafluorethane (R134a) + isobutane (R600a) + 1,1,1,3,3,3-hexafluoropropane (R236fa). These systems were studied as part of a research program financed by the European Union to seek substitutes for 1,2-dichlorotetrafluorethane (R114) in high-temperature heat pump applications. To our knowledge, there are no data available on these systems in the literature.

Experimental

Reagents

2-methyl-propane (isobutane), R600a, CA [75-28-5], supplied by Fluka (for the mixture with R134a) and Air Liquide (for the mixture with R236fa), at a manufacturers' stated purity >99.5% in both cases, 1,1,1,2-tetrafluorethane, R134a, CA [811-97-2] donated by Ausimont (stated purity >99.9%), and 1,1,1,3,3,3-hexafluoropropane, R236fa, CA [690-39-1], supplied by Du Pont (stated purity >99%), were used without further purification. Using an FID detector, our GC analysis revealed no impurities except in the case of the R600a from Air Liquide (0.19% of propane evaluated on the area basis). Using a TCD detector, the following impurities were detected on the area basis: R600a (Fluka) 0.4%; R600a (Air Liquide) 0.4%; R134a 0.07%; R236fa 0.07%.

Apparatus

VLE set-up: this consisted in a VLE view cell equipped with a magnetic pump ensuring intensive circulation of the vapor phase through the liquid phase; the magnetic pump was operated by a motor of smoothly turning frequency. After reaching the equilibrium, the composition of the coexisting liquid and vapor phases was analyzed by an Hewlett Packard 6890 gas chromatograph. The VLE cell was made of stainless steel

(corresponding to AISI 306) and equipped with two windows for observing the mixture during measurements. Gold (purity > 99.99%) O-rings were used to seal the glass windows onto the stainless steel body of the VLE cell. Two miniature valves located at the top and bottom of the VLE cell enabled tiny amounts of liquid and vapor phase samples to be drawn off for GC analysis. The VLE cell and the connected magnetic pump were immersed in a thermostat of about 0.1 m^3 capacity, with windows on a level with the VLE cell. The thermostat was composed of a glass vessel insulated with polyurethane foam and wood. The thermostat could be raised and lowered by a hand lift and all parts of the VLE apparatus were installed in the top of the thermostat. Essentially, the VLE set-up (fig.1) was comparable with those frequently described elsewhere in the literature, so only the description provided by Stryjek et. al. [1] is given, by way of example. The VLE cell with the magnetic pump and thermostat were designed, made and supplied by the Institute of Physical Chemistry of the Polish Academy of Sciences, Warsaw, Poland.

Measurement and control of temperature and pressure: the VLE cell was immersed in a thermostatic bath that enabled the temperature to be stabilized within a margin of error of ± 1 mK throughout the measurements. Temperature control was achieved by means of a computerized PID-controlled system governing a heating element immersed in the bath. Below-ambient temperatures were achieved by means of a cooling coil in which a secondary fluid was circulated from a separate thermostatic bath. A PT100Ω thermoresistance temperature sensor connected to a multimeter enabled the temperature to be measured within an estimated error of 1.5 mK. Pressure was measured using a Bourdon pressure gauge with a quartz spiral which has a precision of 0.003% FS. To ensure an adequate precision over the whole range of expected pressure values, two RUSKA 6000 pressure gauges with a full scale of 600 and 3500 kPa respectively, were connected in parallel. A diaphragm was placed between the pressure gauges and the measuring cell. An inert gas (nitrogen) was used for the pressure gauges.

GC calibration and phase composition measurements: GC calibration mixtures were prepared in bottles made of 0.5 mm thick stainless steel and equipped with a special valve enabling the withdrawal of minute samples for GC calibration. The bottle's total capacity was about 240 cm^3; the tare weight was about 180 g and the maximum pressure was 5 MPa, enabling sample preparation by weighing with a standard analytical balance of 240 g capacity and 0.0001 g resolution. The evaluated instrumental uncertainty in mixture preparation was ± 0.0003 g. Considering the high molecular weight and low boiling temperature of refrigerants, the mixtures can be prepared with a precision that is usually better then ± 0.0001 mole fraction (± 0.0003 in the worst cases, depending on the composition and molecular weight of the mixture components).

Due to the presence of fluorine atoms in two of the compounds being investigated (R134a and R236fa), a careful comparison was made of the findings obtained with two detectors (FID and TCD). This showed that the FID detector is significantly more sensitive and its response is a more linear function of the mixture composition. Here, it is worth mentioning the relative ion efficiency per carbon atom of partially fluorinated hydrocarbons with respect to R600a: 1.0000 for R600a (by definition), 0.7170 for R134a and 0.7983 for R236fa. At least 10 samples of various composition were prepared for each binary system and a composition-dependent slightly non-linear response was evident from the GC data fit. The GC response was continuously recalibrated and small changes in actual GC response due to GC parameter instability were observed and taken into account. During optimization, a very good resolution and short total analysis time in isothermal conditions were obtained. The operating parameters and component retention time for each system are given in table 1. The estimated accuracy of measured composition data is ±0.001 for both vapor and liquid mole fractions.

Method of VLE measurements: after evacuating the previous sample and purging the system, a new sample of one of the mixture component was loaded in the VLE cell.

After equilibrium was reached, the system pressure and temperature were recorded, then the second component of the mixture was added. Again, after reaching equilibrium, temperature and pressure were recorded and the phase composition was analyzed by the GC with a computerized integrator. At least 5 analyses were performed for each phase and the average values were considered as corresponding to the equilibrium values.

Results and discussion

VLE data

Tables 2, 3 and 4 show the *p-T-x-y* data values measured at 293.66 K and 303.68 K for the R134a+R600a system, at 283.62 K and 303.68 K for the R600a+R236fa and at 303.68 K in the case of the R134a+R236fa. The R134a+R236fa system (table 3) was almost ideal - as was to be expected, since the system is composed of two close members of homologous series (ethane and propane) with a similar degree of fluorination (the H:F is 2:4 in R134a and 2:6 in R236fa). On the other hand, both the binaries - R134a+R600a (table 2) and R600a+R236fa (table 4) - composed of hydrocarbon (here R600a) and relatively highly fluorinated R134a and R236fa, exhibited positive homogeneous azeotropes with qualitatively similar courses of deviation from Raoult's law.

Consistency test on experimental findings

Strict thermodynamic conditions for the consistency of high-pressure VLE have been described in the literature [2, 3] and recently various aspects of the problem were discussed by Miklos et al. [4]. The main difficulty in applying such a strict method to VLE analysis lies in the lack of volumetric data. A procedure developed by Bertucco et al. [5] was consequently applied, in which the Redlich-Kwong-Soave equation of state [6, 7] with the Huron-Vidal mixing rules [8] was used with the relevant Margules equation for excess Gibbs free energy (binary mixtures) [9]:

$$\frac{G^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2 - \left(C_{21}x_1 + C_{12}x_2\right)x_1x_2 + \left(D_{21}x_1 + D_{12}x_2\right)x_1^2x_2^2 \qquad (1)$$

and the expression for the activity coefficient related to the component (1) is:

$$\ln\gamma_1 = x_2^2\left[6x_2^5\left(D_{12}-D_{21}\right)-5x_2^4\left(3D_{12}-4D_{21}\right)+4x_2^3\left(C_{12}-C_{21}+3D_{12}-6D_{21}\right)+\right.$$
$$-3x_2^2\left(2C_{12}-3C_{21}-4D_{21}+D_{12}\right)+2x_2\left(A_{12}-A_{21}+C_{12}-3C_{21}-D_{21}\right)+$$
$$\left.+2A_{21}+C_{21}-A_{12}\right] \qquad (2)$$

The advantage of this approach lies in the flexibility in the number of adjustable parameters (A, C, D) in the Margules equation, that can be arbitrarily truncated after either first or next terms. The volumetric properties of both the liquid and the vapor phase result from the EOS being used. In our opinion, however, the method chosen in our cases (pressures below 900 kPa) does not influence the general outcome of the consistency test. The Margules parameters are fitted by minimization of the following objective function:

$$obf = \sum_{i=1}^{N_p}\left[\delta(\Delta P/P)\right]^2 \qquad (3)$$

where N_p is the number of isothermal data points considered, and the residuals on pressure $\delta(\Delta P/P)$ are given by:

$$\delta(\Delta P/P) = \frac{P_{calculated}}{P_{experimental}} - 1 \qquad (4)$$

It is worth noting that, in order to perform a thermodynamic consistency test, it must be possible to get unbiased residuals on pressure, within their experimental uncertainty, with a reasonable number of fitting parameters. The VLE data set is then considered consistent if the residuals on vapor composition δy:

$$\delta y = y_{calculated} - y_{experimental} \qquad (5)$$

are also unbiased and within the estimated experimental margin of error.

Table 5 shows the values for the properties of the compounds that were used to perform the consistency test [10, 11, 12, 13]. Table 6 summarizes the results of the consistency tests and Figure 2 shows an example of the distribution of the pressure and vapor composition residuals.

Conclusions

The test on the experimental set-up for VLE measurements demonstrated that the apparatus was successful and fully applicable. Assuming that experimental errors for x and y are ± 0.001, we are confident that a deviation in y below 0.002 is fully consistent with the model and the procedure involved in the consistency test. New data emerged for the R134a + 600a, R134a + 236fa and R600a + 236fa systems. For two systems, the occurrence of positive azeotropes was revealed.

List of symbols

A, C, D	Margules equation coefficients	T	temperature
G^E	molar excess Gibbs free energy	x	liquid mole fraction
N_p	number of data points	y	vapor mole fraction
obf	objective function	RMS	root mean square deviation
P	pressure	***Greek***	
$r.t.$	retention time	γ	activity coefficient

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TABLES

Table1. GC operating parameters and compound retention times.

System *	*Packing*	*Flow rate (cc/min)*			*Temperature (K)*			*Fluid*	*R.t.(min)*
		N_2	*H_2*	*Air*	*Oven*	*Injector*	*Detector*		
A	Porapak Q	30	55	550	413	413	523	R134a	0.919
								R600a	2.314
B	Porapak R	22	45	450	393	393	523	R134a	1.109
								R236fa	2.275
C	Porapak T	28	45	450	413	413	523	R600a	1.770
								R236fa	2.606

** A: R134a+R600a, B: R134a+R236fa and C: R236fa+R600a.*

Table 2. VLE *(p-T-x-y)* data for the R134a+R600a system at 293.66 K and 303.68 K.

T = 293.66 K		
P (kPa)	x_{R134a}	y_{R134a}
306.7	0.0000	0.0000
426.1	0.0626	0.2822
473.2	0.0970	0.3805
470.1	0.0982	0.3751
478.5	0.1082	0.3853
495.0	0.1238	0.4173
552.4	0.1953	0.4933
569.1	0.2289	0.5182
601.9	0.2969	0.5608
643.6	0.4526	0.6241
655.4	0.5284	0.6481
661.8	0.5680	0.6607
666.6	0.6513	0.6903
669.0	0.7442	0.7295
665.5	0.7977	0.7579
641.4	0.9028	0.8427
580.0	1.0000	1.0000

T = 303.68 K		
P (kPa)	x_{R134a}	y_{R134a}
410.7	0.0000	0.0000
580.8	0.0825	0.3110
649.9	0.1308	0.3994
739.5	0.2239	0.4977
781.3	0.2865	0.5427
854.2	0.4822	0.6298
879.6	0.6230	0.6817
884.3	0.7837	0.7572
877.9	0.8276	0.7861
849.2	0.9133	0.8652
780.9	1.0000	1.0000

Table 3. VLE *(p-T-x-y)* data for the R134a+R236fa system at 283.62 K and 303.68 K.

T = 283.62 K			*T = 303.68 K*		
P (kPa)	x_{R134a}	y_{R134a}	*P (kPa)*	x_{R134a}	y_{R134a}
162.6	0.0000	0.0000	325.8	0.0000	0.0000
190.6	0.1154	0.2358	372.5	0.1101	0.2057
225.2	0.2570	0.4500	441.6	0.2743	0.4404
251.7	0.3627	0.5722	498.5	0.4024	0.5851
284.4	0.4913	0.6940	545.3	0.5085	0.6813
314.3	0.6056	0.7824	588.2	0.6021	0.7590
345.1	0.7219	0.8586	641.1	0.7151	0.8391
383.5	0.8638	0.9366	679.9	0.7942	0.8884
420.7	1.0000	1.0000	730.4	0.8982	0.9475
			780.9	1.0000	1.0000

Table 4. VLE *(p-T-x-y)* data for the R600a+R236fa system at 303.68 K.

T = 303.68 K					
P (kPa)	x_{R600a}	y_{R600a}	*P (kPa)*	x_{R600a}	y_{R600a}
325.8	0.0000	0.0000	535.4	0.5509	0.5766
389.6	0.0612	0.2007	535.2	0.6625	0.6240
436.5	0.1199	0.3023	530.9	0.7148	0.6511
483.3	0.2192	0.4084	517.2	0.8099	0.7073
498.0	0.2645	0.4434	486.5	0.8979	0.7914
513.5	0.3297	0.4818	449.4	0.9579	0.8922
523.2	0.3876	0.5100	410.7	1.0000	1.0000
532.7	0.4897	0.5528			

Table 5. Values of the properties of the considered compounds for consistency test.

Compound	*Critical Temperature (K)*	*Critical Pressure (kPa)*	*Vapor pressure*
R134a	374.21 [10]	4056 [10]	[10]
R600a	408.13 [11]	3648 [11]	[12]
R236fa	403.75 [13]	3180 [13]	this work

Table 6. Results of consistency tests along with a 4 parameters Margules equation.

System	*T (K)*	*δ(ΔP/P)%*		*δy*	
		RMS	*bias*	*RMS*	*bias*
R134a+R600a	293.66	0.306	0.0190	0.0050	0.0006
	303.68	0.142	0.0220	0.0024	0.0005
R134a+R236fa	283.62	0.029	0.0083	0.0018	0.0014
	303.68	0.078	0.0157	0.0021	0.0018
R600a+R236fa	303.68	0.162	0.0244	0.0046	0.0009

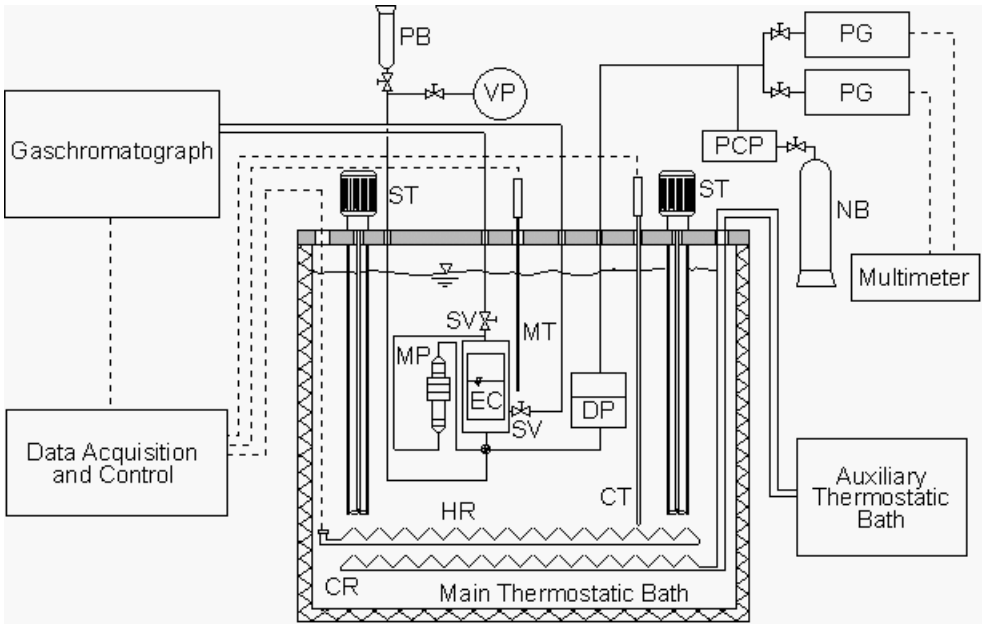

Figure 1: Schematic diagram of the apparatus. Components are labeled as follows: cooler (CR), resistance thermometer for temperature control (CT), diaphragm (DP), equilibrium cell (EC), heating resistor (HR), magnetic pump (MP), resistance thermometer for temperature measurement (MT), nitrogen bottle (NB), pure refrigerant bottle (PB), pressure control pack (PCP), pressure gauge (PG), stirrer (ST), sampling valve (SV), vacuum pump (VP).

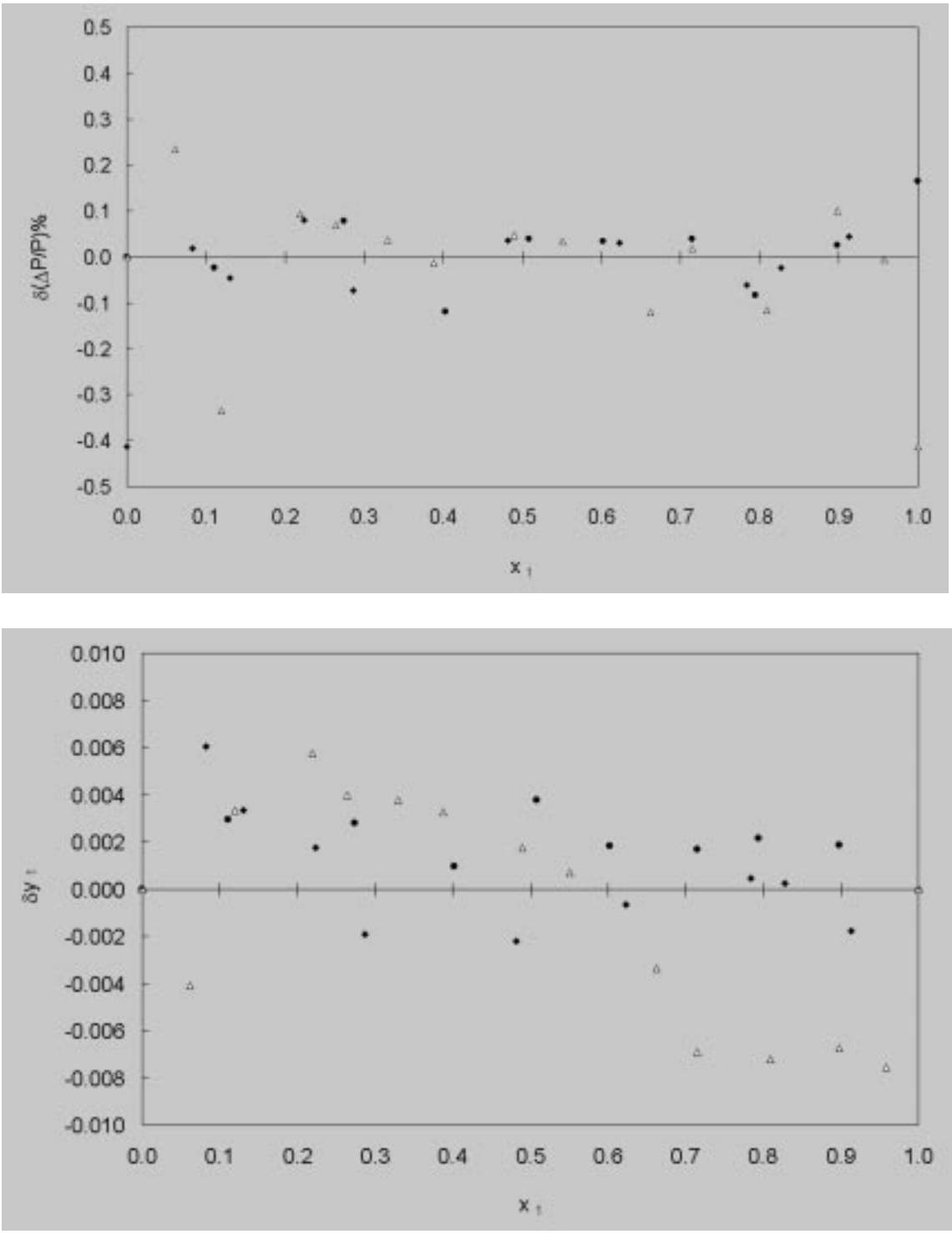

Figure 2: Residuals of pressure (a) and vapor composition (b) for the R134a(1)+R600a(2) [◆], R134a(1)+R236fa(2) [●] and R600a(1)+R236fa(2) [△] systems at 303.68 K for checking thermodynamic consistency.