On the influence of adsorption on *PVT* measurements in the gaseous phase [1]

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ABSTRACT

The *PVT* measurements of 1,1,1,2-tetrafluoroethane ($C_2H_2F_4$, HFC-134a) and its blend with octofluoropropane (C_3H_8, FC-218) have been performed in the gas phase near the dew curve. The experimental data were obtained by variable volume and vibrating tube methods. The discrepancies in the behavior of isotherms from their classical behavior were experimentally observed. It was found that the phase transition does not go to completion at the single point of the thermodynamic surface, but extends over a limited range of parameters. Obtained results are in accordance with a concept of adsorption of the vapor sample on the surface of the experimental cell. Increasing of adsorption at the parameters close to the condensation is the cause of capillary condensation of the sample at the walls of the cell that initiates earlier phase transition. The ranges of diffuse phase transitions were determined for 1,1,1,2-tetrtafluoroethane as well as for its mixture with octofluoropropane at different thermodynamic parameters.

The influence of selective adsorption on the change in the parameters of phase transition of the mixture 1,1,1,2-tetrafluoroethane/octofluoropropane was also experimentally studied.

KEY WORDS: adsorption, capillary condensation, phase transition, *PVT* measurements

1. INTRODUCTION

Basic *PVT* methods such as constant volume and variable volume methods, vibrating tube method and others provide high accuracy of experimental data[1] in a relatively wide range of thermodynamic parameters. However due to some methodological uncertainties at the parameters near phase transitions, even careful measurements lead to discrepancies in the behavior of experimental iso-lines from their classical behavior. Results of the present and some other experimental works reveal diffuse character of the transition parameters that cannot be attributed to the finite size of the cell or fluctuation phenomena [1]. Recent thermodynamic generalizations of phase transitions [1,2] are based on the use of the additional function $L(x)$ which defines the relative amount of the sample transferred to the new phase at the single-phase volumetric conditions. According to this method, thermodynamic potential of the system in the region of phase transition can be expressed by the following equation

$$Y(x) = Y^{(\alpha)}(x) + \Delta Y(x) L(x) \qquad (1)$$

where $\Delta Y(x)$ is the effective leap in the thermodynamic function $Y(x)$. $Y^{(\alpha)}(x)$ is a thermodynamic potential of the phase α.

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[1]For the most of *PVT* methods the ranges of experimental uncertainties are within 0.005-0.05 K, 0.05-0.3% and 0.1-0.5% for the temperature, pressure and density measurements, respectively.

In case of diffuse phase transition, function *L(x)* can be written

$$L(x) = \begin{cases} 0 & x < x_1 \\ L_{1,2}(x) & x_1 < x < x_2 \\ 1 & x > x_2 \end{cases} \qquad (2)$$

where x_1 and x_2 are parameters at the beginning and the end of phase transition.

Just as classical phase transition behavior assumes $L_{1,2}(x) = 0$ and equality of arguments x_1 and x_2.

Non-thermodynamic methods of determination of the function $L_{1,2}(x)$ are considered in [1]. However $L_{1,2}(x)$ is related to the whole thermodynamic system (sample and experimental cell) and, therefore, vary for different experimental conditions. As shown in the present study the influence of experimental conditions on the change in the parameters of phase transitions may be significant. The paper presents the results of *PVT* measurements of 1,1,1,2-tetrafluoroethane and its blend with octofluoropropane near the dew curve at different thermodynamic parameters. Temperature and concentration changes of phase transition ranges were experimentally observed and were accounted for by the surface effects, namely by the physical adsorption of the sample and its capillary condensation on the inner surface of the experimental cell.

2. DIFFUSE PHASE TRANSITIONS FOR THE PURE COMPOUND

Two different methods, variable volume [3] and vibrating tube method [4], were applied for the experimental study of *PVT* properties of 1,1,1,2-tetrafluoroethane in the vapor phase near the saturation. An example of typical experimental isotherm of 1,1,1,2-tetrafluoroethane is given in Fig. 1. Runs were conducted along isotherm starting from point 1. The beginning of phase transition was registered at point 4. It was characterized by

spontaneously increasing pressure and density of the sample and by difficulty or even unfeasibility to keep a thermodynamic equilibrium. Phase transition was accompanied by visually observed condensation of the vapor phase at point 5 (variable volume cell). The curvature of the experimental isotherms in the vapor phase increased monotonously as the dew curve is approached. It did not go to completion at the dew point, but extended over a range from points 4 to 7. Classic behavior of the isotherm was observed later, at the range between points 7 and 8. Obtained results were qualitatively similar for both experimental methods. Deviations of the experimental vapor pressures $P_{ph.tr.}$, at the beginning of phase transition, from the reference values P_s for 1,1,1,2-tetrafluoroethane are given in Table 1.

The observed characteristic feature of the behavior of the experimental isotherms is a result of different factors such as impurities of investigated sample, effect of external fields and physical adsorption of the substance on the surface surrounding it. Adsorption plays the main role for vapor-liquid phase transition. It originates a new phase in experimental cell at the parameters corresponding to the vapor phase, i.e., it can produce a diffuse phase transition as a result of capillary condensation in the microroughness of the wall surfaces. Capillary condensation occurs at vapor pressures below the saturation pressure, starting at the parameters when the microcapillaries of the cell are covered by a layer of adsorbed molecules [1]. The presence of the liquid phase condensed into the micropores cannot be observed at this stage, but it can be recorded by pressure-measurement facilities (point 4). Quantitative difference between the results obtained by variable volume and vibrating tube methods may be accounted for by the difference of the materials of the experimental cell and techniques used for approaching to the condensation line. The variable volume cell was made of molibden glass with less microroughness on the inner surface than the stainless steel

vibrating tube has. Therefore, the variable volume cell is less effective on the phase transition. Influence of employed experimental techniques on the change of transition parameters is also different. The pressure was applied to the vapor sample through the pressure-transfer medium (mercury) in a variable volume method. In the second method, the pressure was increased by introducing additional amount of the sample into the vibrating tube. Thus, approaching to saturation in both of experimental methods included mechanical disturbance of the sample that effected on the results of the measurements.

3. DIFFUSE PHASE TRANSITIONS FOR THE BINARY MIXTURE

PVT properties near phase transitions were studied for the mixture of 1,1,1,2-tetrafluoroethane and octofluoropropane by variable volume method. The experimental results on this system are summarized in Tables 2 and 3. One of the studied isotherms is presented at the Fig. 2 for convenience in analysis of obtained results. One can see that ranges of phase transitions are different depending on concentration of the mixture. Such difference may be explained by selective character of adsorption of the components on the surface of the experimental cell. Due to physical adsorption increases asymptotically at the saturation [5], the adsorption of low vapor pressure component is predominant. It causes earlier capillary condensation of one of the components accompanied by concentration changes of the volumetric vapor phase. In our measurements, the composition of the investigated mixture was changed near the saturation because of selective adsorption of 1,1,1,2-tetrafluoroethane. The difference between P'' (dew point pressure at initial concentration X) and $P''_{ads.}$ (pressure at concentration $X_{ads.}$ which is changed by molecular adsorption) is determined by the slope of isotherm in P-X diagram. Condition $P''_{ads.} < P''$ (X=0.751) leads to expansion of the parameters of diffuse phase transition, but condition

$P''_{ads.} > P''$ (X=0.266 and X=0.358) leads to their reduction. Slope of isotherms in P-X diagram (or derivative $\left(\partial P''/\partial X\right)_T$) also determines quantity of the change of phase transition parameters. Even small changes of the volume concentration of the mixture X=0.751 lead to a considerable increase of difference $\left(P'' - P''_{ads.}\right)$. Derivative $\left(\partial P''/\partial X\right)_T$ at this concentration is not equal to zero and the influence of selective adsorption on phase transition is very high. At concentration of azeotrope X=0.419, derivative $\left(\partial P''/\partial X\right)_T \to 0$. It means that concentration changes caused by selective adsorption have little or no influence on the value of dew point pressure $\left(P'' \approx P''_{ads.}\right)$. Thus, at thermodynamic parameters $\left(\partial P''/\partial X\right)_T \approx 0$ the influence of selective character of molecular adsorption on the change of parameters of transition is insignificant. It can be confirmed by comparing ranges of phase transitions for azeotropic composition of the mixture and pure 1,1,1,2-tetrafluoroethane (Table 2).

4. CONCLUSION

PVT behavior of mixture 1,1,1,2-tetrafluoroethane/octofluoropropane was experimentally studied at the phase transitions regions. The diffuse character of phase transitions was determined. Obtained results are in accordance with the concept of early capillary condensation caused by adsorption effects on the inner surface of the cell. Experimentally determined reduction of diffuse phase transitions with increasing of temperature is a result of decreasing physical adsorption. At constant temperature the character and quantity of the change of phase transition parameters are determined by selective adsorption and by the value of derivative $\left(\partial P''/\partial X\right)_T$ at any point on the dew curve. The conclusions made are very important for examining methodological aspects of investigating *PVTX* properties in the phase transition regions as well as for analysis of the experimental results with a view to reducing them to uniform thermodynamic conditions.

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Table 1. Deviations of the experimental vapor pressures $P_{ph.tr.}$, at the beginning of phase transition, from the reference values P_s for 1,1,1,2-tetrafluoroethane

Vibrating tube method		Variable volume method	
T, K	δP^*, %	T, K	δP^*, %
273.15	-3.33	309.76	-1.55
303.15	-2.20	321.54	-1.16
333.15	-1.79	334.70	-0.80

$\delta P = 100(P_{ph.tr.} - P_s)/ P_s$

Table 2. Deviations of the experimental vapor pressures $P''_{ph.tr.}$, at the beginning of phase transition, from dew point pressures P'' for the mixture 1,1,1,2-tetrafluoroethane/ octofluoropropane

T, K	$\delta P=100(P''_{ph.tr.}-P'')/P''$, %				
	X=0.266	X=0.358	X=0.419	X=0.751	X=1.0
285.73	-1.69	-0.92	-2.26	-8.42	-
309.76	-1.15	-0.53	-1.50	-7.66	-1.55
320.77	-0.94	-0.45	-1.19	-5.78	-
321.54	-	-	-	-	-1.16
331.78	-0.22	-0.34	-	-3.98	-
334.70	-	-	-	-	-0.80

X-mol.% of 1,1,1,2-tetrafluoroethane

Table 3. *PVT* properties of the mixture 1,1,1,2-tetrafluoroethane/octofluoropropane in the range of phase transitions

X	*T*, K	*P*, MPa	ρ, kg m^{-3}	*X*	*T*, K	*P*, MPa	ρ, kg m^{-3}
0.266	285.73	0.6740	56.69	0.266	309.76	1.3582	195.49
0.266	285.73	0.6798	57.17	0.266	309.76	1.3611	280.72
0.266	285.73	0.6836	57.53	0.266	309.76	1.3656	319.47
0.266	285.73	0.6874	57.91	0.266	309.76	1.3674*	1201.9*
0.266	285.73	0.6912	58.30	0.266	320.77	1.7208	162.75
0.266	285.73	0.6976	58.89	0.266	320.77	1.7267	164.05
0.266	285.73	0.7016	59.39	0.266	320.77	1.7325	164.99
0.266	285.73	0.7051	61.04	0.266	320.77	1.7364	165.67
0.266	285.73	0.7103**	71.30**	0.266	320.77	1.7403	166.36
0.266	285.73	0.7138	98.78	0.266	320.77	1.7442	167.01
0.266	285.73	0.7153	127.73	0.266	320.77	1.7501	168.10
0.266	285.73	0.7165	185.91	0.266	320.77	1.7559	171.00
0.266	285.73	0.7176	277.10	0.266	320.77	1.7633**	201.06**
0.266	285.73	0.7175*	1349.1*	0.266	320.77	1.7664	211.40
0.266	309.76	1.2923	114.13	0.266	320.77	1.7717	271.36
0.266	309.76	1.3034	115.78	0.266	320.77	1.7724	293.22
0.266	309.76	1.3136	117.16	0.266	320.77	1.7809*	1120.9*
0.266	309.76	1.3231	118.50	0.266	331.78	2.2270	236.60
0.266	309.76	1.3309	119.62	0.266	331.78	2.2348	239.14
0.266	309.76	1.3367	120.49	0.266	331.78	2.2426	241.74
0.266	309.76	1.3426	121.38	0.266	331.78	2.2509	244.33
0.266	309.76	1.3480	127.55	0.266	331.78	2.2548	245.68
0.266	309.76	1.3515**	141.44**	0.266	331.78	2.2587	247.12
0.266	309.76	1.3538	154.96	0.266	331.78	2.2643**	264.68**
0.266	309.76	1.3560	172.04	0.266	331.78	2.2662	274.77

Table 3. (Continued)

X	*T*, K	*P*, MPa	ρ, kg m^{-3}	*X*	*T*, K	*P*, MPa	ρ, kg m^{-3}
0.266	331.78	2.2679	288.53	0.358	309.76	1.3748	130.58
0.266	331.78	2.2688	295.46	0.358	309.76	1.3769	157.95
0.266	331.78	2.2851*	-	0.358	309.76	1.3788	214.66
0.358	285.73	0.6960	55.92	0.358	309.76	1.3784	293.65
0.358	285.73	0.6998	56.28	0.358	309.76	1.3807*	1199.1*
0.358	285.73	0.7035	56.66	0.358	320.77	1.7778	161.38
0.358	285.73	0.7072	57.04	0.358	320.77	1.7797	162.09
0.358	285.73	0.7110	57.43	0.358	320.77	1.7816	162.81
0.358	285.73	0.7148	57.86	0.358	320.77	1.7836	163.43
0.358	285.73	0.7182	59.24	0.358	320.77	1.7855	164.03
0.358	285.73	0.7204**	64.96**	0.358	320.77	1.7865	164.51
0.358	285.73	0.7225	95.50	0.358	320.77	1.7874	165.21
0.358	285.73	0.7232	162.40	0.358	320.77	1.7884	166.15
0.358	285.73	0.7221	260.63	0.358	320.77	1.7894**	169.13**
0.358	285.73	0.7218	312.47	0.358	320.77	1.7903	171.86
0.358	285.73	0.7248*	1344.6*	0.358	320.77	1.7914	175.38
0.358	309.76	1.3635	117.11	0.358	320.77	1.7939	190.33
0.358	309.76	1.3658	117.37	0.358	320.77	1.7960	222.58
0.358	309.76	1.3674	117.68	0.358	320.77	1.7974	251.47
0.358	309.76	1.3693	117.94	0.358	320.77	1.7985	313.63
0.358	309.76	1.3703	118.12	0.358	320.77	1.8006*	1112.1*
0.358	309.76	1.3712	118.62	0.419	285.73	0.5890	48.94
0.358	309.76	1.3721	119.43	0.419	285.73	0.6380	49.44
0.358	309.76	1.3732**	124.32**	0.419	285.73	0.6533	50.38
0.358	309.76	1.3733	124.68	0.419	285.73	0.6610	51.11
0.358	309.76	1.3747	131.75	0.419	285.73	0.6687	51.89

Table 3. (Continued)

X	*T*, K	*P*, MPa	ρ, kg m^{-3}	*X*	*T*, K	*P*, MPa	ρ, kg m^{-3}
0.419	285.73	0.7187**	110.88**	0.419	320.77	1.7769	165.79
0.419	285.73	0.7203	148.14	0.419	320.77	1.7876	194.36
0.419	285.73	0.7230	196.17	0.419	320.77	1.7940	229.00
0.419	285.73	0.7236	215.36	0.419	320.77	1.7970	256.01
0.419	285.73	0.7234	228.02	0.419	320.77	1.7975*	-
0.419	285.73	0.7235*	-	0.751	285.73	0.5673	37.41
0.419	309.76	1.2779	102.42	0.751	285.73	0.5691	37.77
0.419	309.76	1.2935	104.24	0.751	285.73	0.5708	38.16
0.419	309.76	1.3091	106.15	0.751	285.73	0.5738	39.43
0.419	309.76	1.3325	109.13	0.751	285.73	0.5964**	55.05**
0.419	309.76	1.3480	112.04	0.751	285.73	0.6006	57.81
0.419	309.76	1.3557	115.08	0.751	285.73	0.6239	89.63
0.419	309.76	1.3576	116.17	0.751	285.73	0.6376	132.44
0.419	309.76	1.3704**	140.94**	0.751	285.73	0.6453	184.44
0.419	309.76	1.3729	156.85	0.751	285.73	0.6493	220.08
0.419	309.76	1.3769	200.04	0.751	285.73	0.6572*	1286.8*
0.419	309.76	1.3782	234.59	0.751	320.77	1.4718	91.36
0.419	309.76	1.3783	249.13	0.751	320.77	1.4815	92.30
0.419	309.76	1.3783*	-	0.751	320.77	1.4912	93.26
0.419	320.77	1.7146	147.12	0.751	320.77	1.5009	94.29
0.419	320.77	1.7302	149.68	0.751	320.77	1.5663**	142.39**
0.419	320.77	1.7381	150.73	0.751	320.77	1.5845	175.75
0.419	320.77	1.7458	152.14	0.751	320.77	1.5992	215.40
0.419	320.77	1.7537	153.32	0.751	320.77	1.6654*	1099.9*
0.419	320.77	1.7615	154.67	0.751	331.78	1.9200	124.61
0.419	320.77	1.7692**	158.99**	0.751	331.78	1.9297	125.70

Table 3. (Continued)

X	T, K	P, MPa	ρ, kg m^{-3}	X	T, K	P, MPa	ρ, kg m^{-3}
0.751	331.78	1.9395	126.87	0.751	331.78	2.0300	184.30
0.751	331.78	1.9492	128.06	0.751	331.78	2.0432	210.73
0.751	331.78	1.9594	129.41	0.751	331.78	2.0567	248.77
0.751	331.78	1.9692	130.65	0.751	331.78	2.0568	252.99
0.751	331.78	2.0164**	165.30**	0.751	331.78	2.1103*	1027.7*

* - bubble point; ** - parameters of visual observation of condensed phase.

FIGURE CAPTIONS

Fig. 1. Typical experimental isotherm at the phase transition range: 1-8 are experimental points

Fig. 2. Phase transition regions at different concentrations of the mixture 1,1,1,2-tetrafluoroethane/octofluoropropane

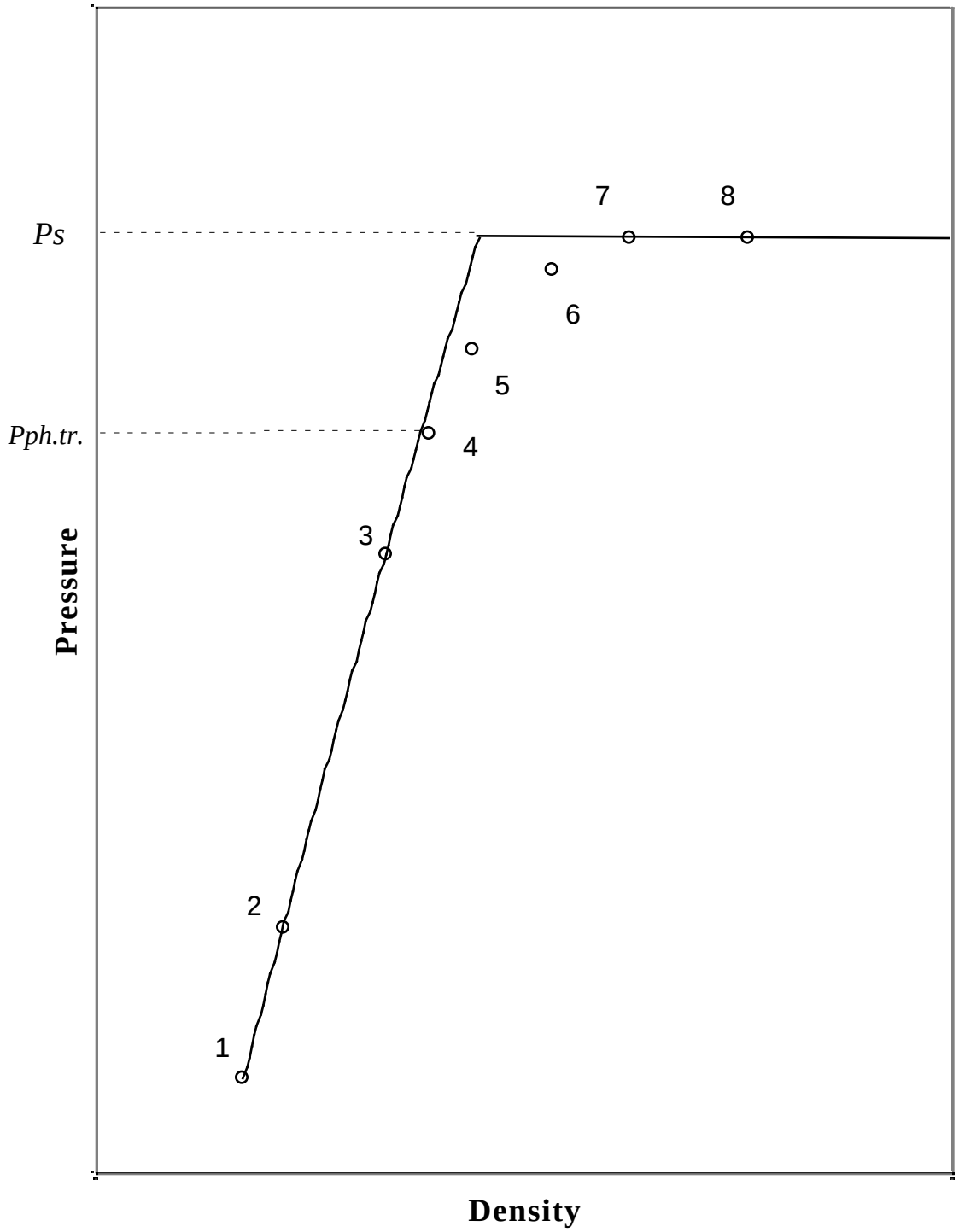

Fig.1

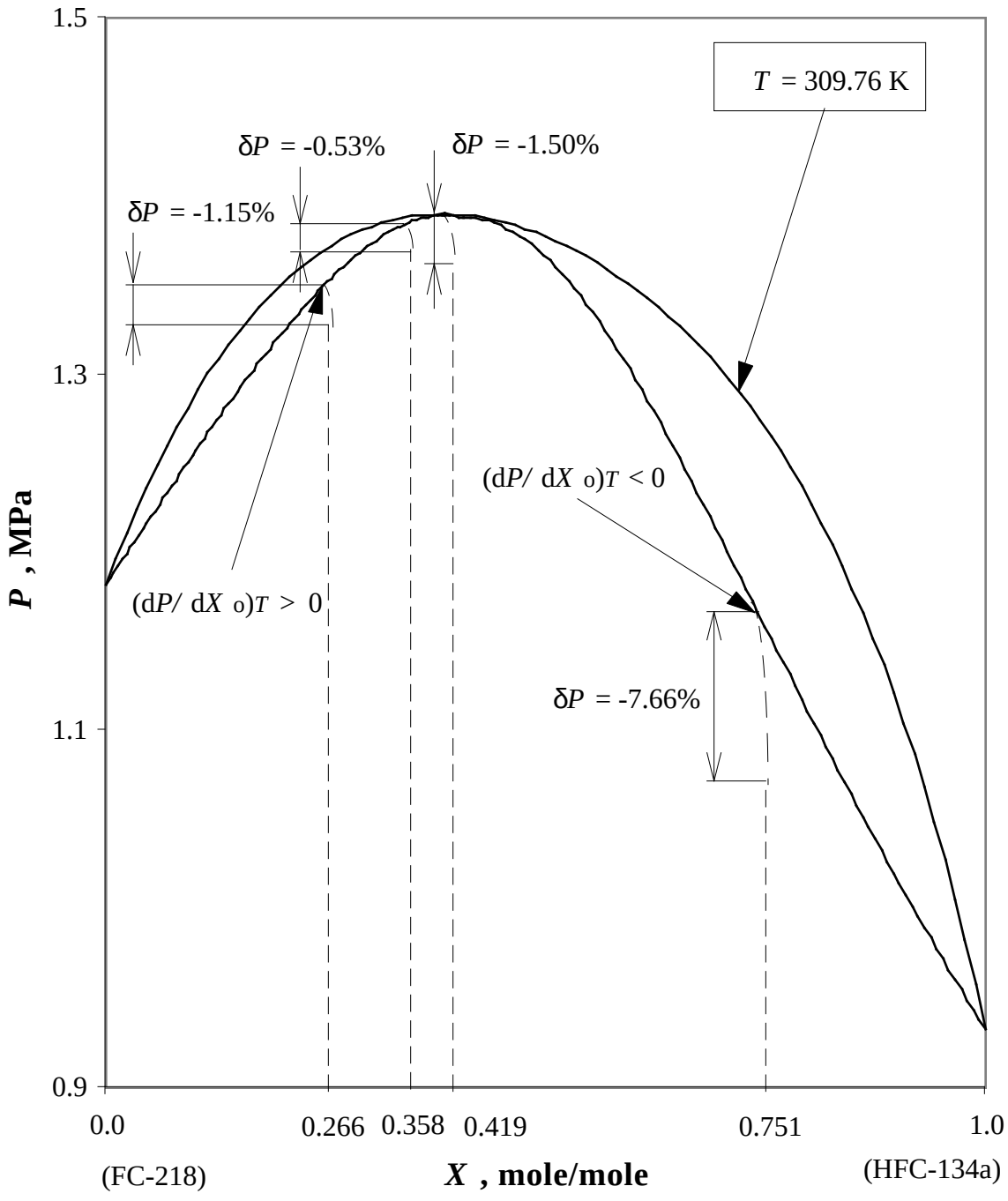
1.5
1.3
1.1
0.9
P , MPa
T = 309.76 K
δP = -0.53%
δP = -1.50%
δP = -1.15%
(dP/ dX o)T < 0
(dP/ dX o)T > 0
δP = -7.66%
0.0
0.266
0.358
0.419
0.751
1.0
(FC-218)
X , mole/mole
(HFC-134a)

Fig. 2