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DETERMINATION OF THE CONCENTRATION OF GASES BY MEASUREMENT OF PRESSURE

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ABSTRACT

For the determination of the concentration of gases by means of pressure measurement, a precise equation of state is given by which analysis can be carried out within an accuracy of 10 ppm. The parameters of the equation of state are explicitely reported for carbon dioxide, argon, and helium.

INTRODUCTION

The determination of the density or concentration of pure gases is usually carried out by a precise and simple pressure measurement as a standard procedure. Densities and concentrations are thereof obtained by use of an equation of state. The precision of this determination method is generally limited by the validity of the equation. Gases with low densities are precisely described by the ideal gas law. However, an equation of general validity doesn't exist for gases with high densities[1-4] .

RESULTS AND DISCUSSION

In other context we found, that pure gases form three different structures with increasing density: at low density a structure with nearly free motion of the particles, at higher density a structure which is characterized by the contact of particles, and at high density a densely packed state. The transition between these structures is rather abrupt. Therefore, gases are described best by three different equations corresponding to the three different structures.

For the concentration region I, at low densities, the pressure as a function of concentration is described best by equation (1), in which c is the molar

$$p = F_p \cdot \ln (c + c^*) + p' \qquad (1)$$

$$\ln (p + p^*) = F_c \cdot c + c^o \qquad (2)$$

concentration of the gas (the density can be calculated thereof in the usual manner). p is the pressure and F_p and c* are the parameters of the equation. The additional parameter p' is zero in region I. The precise validity of eq. (1) is demonstrated by fig. 1 in which a linear correlation between p and ln (c/c* + 1) is shown for CO_2 at 75.260°C on the basis of the precise measurements of A.Michels and C.Michels[5]. A straight line is obtained with a correlation factor of 0.999 998 (10 points). The F_p value is 133.4 at and the c* value 4.59 $mol \cdot l^{-1}$. The latter is calculated by an iterative procedure.

Eq. (1) holds up to a critical concentration c_k(I-II) of 3.1 $mol \cdot l^{-1}$. With higher concentrations, there is an abrupt change of medium structure. In this case (region II) eq. (1) holds too, but with different parameters F_p and c*, and the p' value is not zero.

At the even higher concentration c_k(II-III) of 10 $mol \cdot l^{-1}$ a second change in medium structure is observed. This high density region III is described by eq. (2). F_c, p*, and c^o are the parameters of the equation. The formation of a liquid phase is due to a limited miscibility between the structures of region II and III. Therefore, the equations hold until the second phase is formed. On the basis of these results the complete diagram of the liquid and gaseous state of

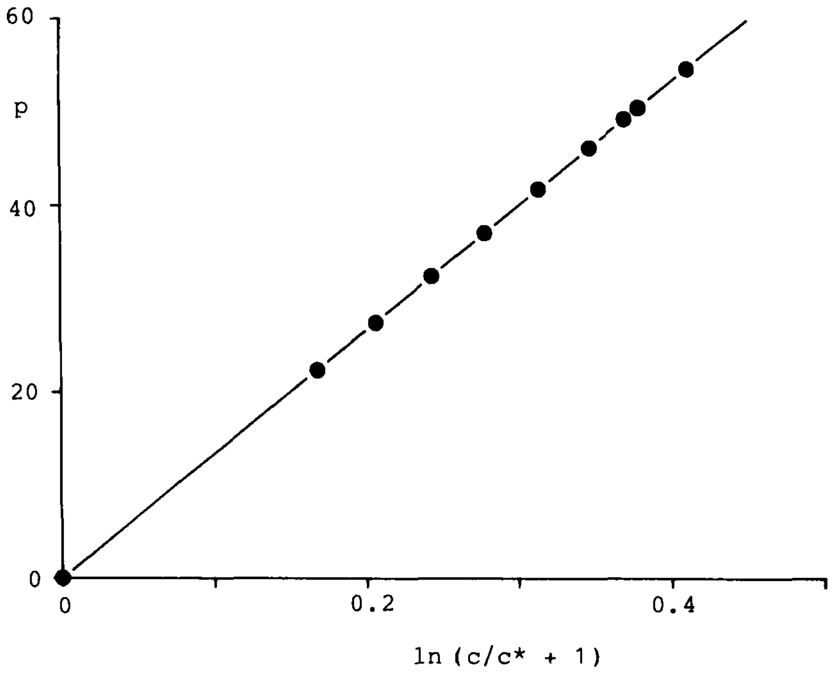

FIG. 1: Linear correlation between p and ln $(c/c^* + 1)$ according to eq. (1) (CO_2 at 75.260°C, $c < 3.1$ mol•l^{-1}).

CO_2 can be drawn, as shown in fig. 2. The parameters of the eq. (1) and (2) are given in Table 1. The gases argon and helium are described in the same manner as carbondioxide - see Tables 2 and 3.

TEMPERATURE DEPENDENCE OF PARAMETERS

The c_k-values are essentially independent of temperature. For the other parameters a linear interpolation between the experimental data of Tables 1 to 3

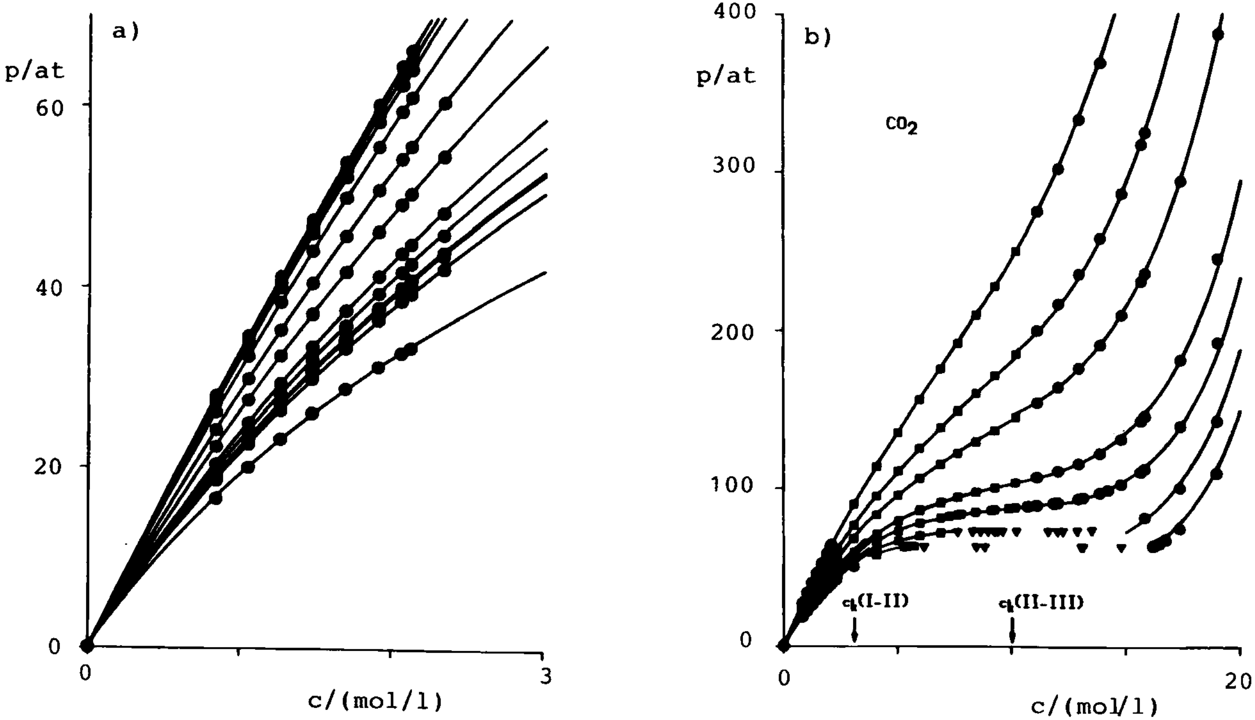

FIG. 2: Diagram of state of CO_2 - pressure measurements are taken from lit[5] - curves are calculated by means of eq. (1) and (2). For clearness the measurements at very high pressure are omitted, but have been taken into account for the calculation of the curves. Temperatures: 25, 32, 40, 49, 75, 99, and 139°C (see tab.1) $c_k(I\text{-}II) \approx 3.1$, $c_k(II\text{-}III) \approx 10\ mol \cdot l^{-1}$. - a) Region I. - b) Region I, II, and III.

TABLE 1

Isothermes of carbondioxide[5] analysed by the use of eq. (1) to (3) - all values in at and mol/l respectively.

Temp. [°C]	region I		region II			region III	
	F_p	$r^{a)}$	F_p	$r^{a)}$	F_c	c^o	$r^{a)}$
	c^*	$N^{b)}$	c^*	$N^{b)}$	p^*	p_{max} c)	$N^{b)}$
0	40.9	0.999 939					
	1.66	9				33.4	
25.070 and	63.4	0.999 973	4.94	0.999 998 7	0.390	-3.09	0.999 377
25.053	2.45	10	-3.42	7	-37.8	865	16
29.900 and	68.7	0.999 977	5.44	0.999 587	0.366	-2.42	0.999 234
29.929	2.63	9	-3.50	6	-47.5	927	7
31.013 and	70.0	0.999 980	8.02	0.999 326	0.360	-2.26	0.999 316
31.037	2.68	10	-3.05	6	-49.2	942	7
32.054 and	71.2	0.999 981	15.3	0.999 704	0.355	-2.14	0.999 378
32.075	2.71	10	-1.79	6	-51.0	955	7
40.085 and	80.6	0.999 986	11.4	0.999 389	0.371	-2.40	0.999 187
40.105	3.02	10	-3.07	16	-81.3	1057	13
49.712	93.6	0.999 992	25.8	0.999 967	0.321	-1.12	0.999 520
	3.43	10	-1.66	9	-94.8	1698	14

75.260	133.4 4.59	0.999 998 10	125.3 5.69	0.999 843 9	0.258 -119.2	0.694 2072	0.999 939 13
99.767	181.4 5.88	0.999 999 5 10	326.4 15.7	0.999 939 7	0.225 -131.5	1.714 2420	0.999 932 14
125.007	243 7.40	0.999 999 9 10	1615 77.8	0.999 941 6	0.205 -141.1	2.38 2772	0.999 938 14
139.832	293 8.63	0.999 999 9 10	1849 78.7	0.999 996 5	0.141 -69.8	3.76 459	0.999 912 10
145.049	319 9.32	0.999 999 9 10	1931 78.74	0.999 982 5	0.146 -80.0	3.69 478	0.999 956 9
150.140	334 9.63	0.999 999 9 10	2008 78.74	0.999 967 5	0.191 -146.2	2.87 3117	0.999 947 14

a) Correlation factor obtained by use of the corresponding equation. - b) Number of points. - c) Maximum pressure.

TABLE 2

Isothermes of argon[6] analysed by the use of eq. (1) to (3) - all values in at and mol/l respectively.

Temp. [°C]	region I		region II		region III		
	F_p	$r^{a)}$	F_p	$r^{a)}$	F_c	c^o	$r^{a)}$
	c^*	$N^{b)}$	c^*	$N^{b)}$	p^*	$p_{max}^{c)}$	$N^{b)}$
-140	32.0	0.999 975			0.312	-3.76	0.999 972
	2.79	10			51.2	150	13
-135	38.6	0.999 991			0.317	-3.78	0.999 931
	3.30	10			21.1	200	16
-130	35.1	0.999 936			0.322	-3.82	0.999 872
	2.75	12			-5.38	222	16
-125	42.28	0.999 968			0.342	-4.23	0.999 293
	3.27	12			-31.7	271	18
-122.5	36.4	0.999 782			0.344	-4.24	0.999 019
	2.58	14			-41.8	300	20
-110	53.9	0.999 919	228	0.999 435	0.257	-1.47	0.999 881
	3.70	19	80	3	-64.4	416	23
-100	63.2	0.999 905	422	0.999 918	0.215	-0.0556	0.999 848
	4.00	19	90	4	-74.4	450	21

-85	105 6.58	0.999 993 19	605 80	0.999 981 4	0.181 -84.6	1.16 600	0.999 870 22
-70	159 9.48	0.999 999 7 20	838 80	0.999 999 4	0.161 -90.2	1.94 700	0.999 891 23
-50	268 14.8	0.999 996 21	1150 80	0.999 994 4	0.144 -91.5	2.65 857	0.999 910 25
-25	510 25.7	0.999 991 22	1600 84	0.999 983 4	0.121 -82.9	3.31 1058	0.999 893 27
0	1052 48.3	0.999 984 22	2048 86.2	0.999 871 5	0.124 -87.9	3.62 2500	0.999 927 35
50	2974 111	0.999 920 9	2909 86	0.999 993 3	0.111 -61.7	4.28 2000	0.999 965 17
75	4754 166	0.999 671 9	3353 80	0.999 977 3	0.106 -39.2	4.54 2000	0.999 971 17

(Continued)

TABLE 2 (Continued)

Temp. [^{o}C]	region I		region II			region III	
	F_p c^*	$r^{a)}$ $N^{b)}$	F_p c^*	$r^{a)}$ $N^{b)}$	F_c p^*	c^o $p_{max}{}^{c)}$	$r^{a)}$ $N^{b)}$
100	15700 500	0.999 999 9	4020 94	0.999 999 3	0.103 -16.8	4.75 2500	0.999 963 18
125	28700 839	0.999 999 9	4690 100	0.999 995 4	0.0985 9.45	4.96 2000	0.999 981 15
150	30800 839	0.999 999 9	5470 110	0.999 864 4	0.0958 34.8	5124 2150	0.999 986 15

a) Correlation factor obtained by use of the corresponding equation. - b) Number of points. - c) Maximum pressure. - d) The measurements near by the region with two phases give larger deviations and are therefore omitted - there are only few measurements in region II and so the calculated parameters have larger uncertainties.

TABLE 3

Isothermes of helium[9] analysed by use of eq. (1) - all values in at and mol/l, respectively.

Temp. [K]	F_p	c*	$r^{a)}$	$N^{b)}$	$p_{max}^{c)}$
2.610	0.623	2.87	0.999 991	18	0.116
3.105	0.862	3.34	0.999 999	6	0.245
3.721	1.113	3.51	0.999 984	8	0.548
4.245	1.328	3.56	0.999 916	19	0.954

a) Correlation factor obtained by the use of eq. (1). - b) Number of points. - c) Maximum pressure.

is sufficiently accurate for most applications. If even higher precision is required, the proportionality of the parameters with a power of the absolute temperature T can be used. This is explicitely done for CO_2 in region I, where the parameters can be determined with high precision. The temperature dependence is given by eq. (3) and (4). The constants F

$$F_p = a_F \cdot T^{\alpha F} \qquad (3)$$

$$c^* = a_c \cdot T^{\alpha c} \qquad (4)$$

and αc are obtained by plots of ln F_p vers. ln T and ln c* vers. ln T. Plots of F_p vers. $T^{\alpha F}$ and c* vers. $T^{\alpha c}$ are given by fig. 3. Straight lines are obtained with correlation factors $r = 0.999\ 7$ and $r = 0.999\ 5$ (13 points). The intercepts are very small and can be omitted in most cases. The temperature dependence of the parameters in region II and III can be described in the same manner as in region I with the same type of equations as (3) or (4).

DETERMINATION OF CRITICAL CONCENTRATIONS c_k

The determination of c_k(I-II) and c_k(II-III) is important for the practical use of eq. (1) and (2). The clue for the determination of c_k is the fact that the correlation according to either eq. (1) or (2) rapidly turns bad when a c_k value is exceeded. This is shown in fig. 4 where the correlation factor is plotted vers. the highest concentration which is taken into account. The point of inflection in fig. 4 gives a c_k(I-II) value of 3.1 $\text{mol}\cdot\text{l}^{-1}$. The c_k(II-III) can be obtained in the same manner starting with the highest concentration and going stepwise to lower concentrations. The so obtained c_k values can be verified by the analogous use of region II.

The point of inflection is more pronounced at lower temperatures, but can easily be localized even at high temperatures. Measurements with lower accuracy give the same type of plot as fig. 4.

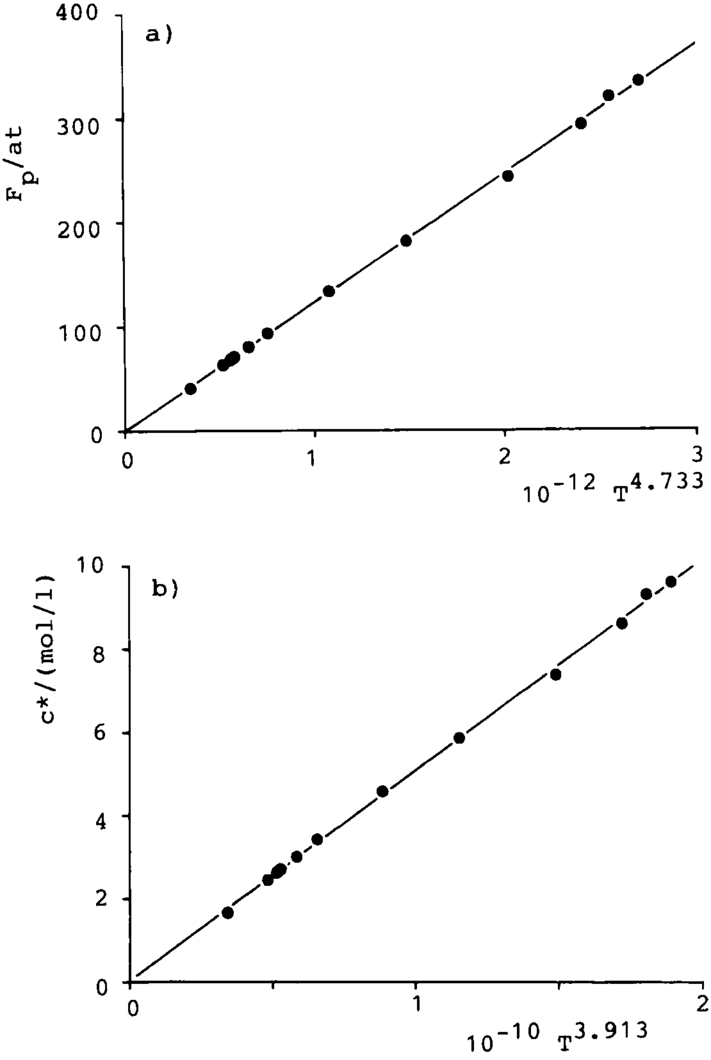

FIG. 3: Temperature dependence of the parameters F_p and c* of carbon dioxide, region I. - a) Plot of F_p vers. $T^{4.73}$ ($a_F = 1.230 \cdot 10^{-10}$, intercept: 0.049 at). - b) Plot of c* vers. $T^{3.913}$ ($a_c = 5.049 \cdot 10^{-10}$, intercept: 0.036 mol$\cdot$l^{-1}).

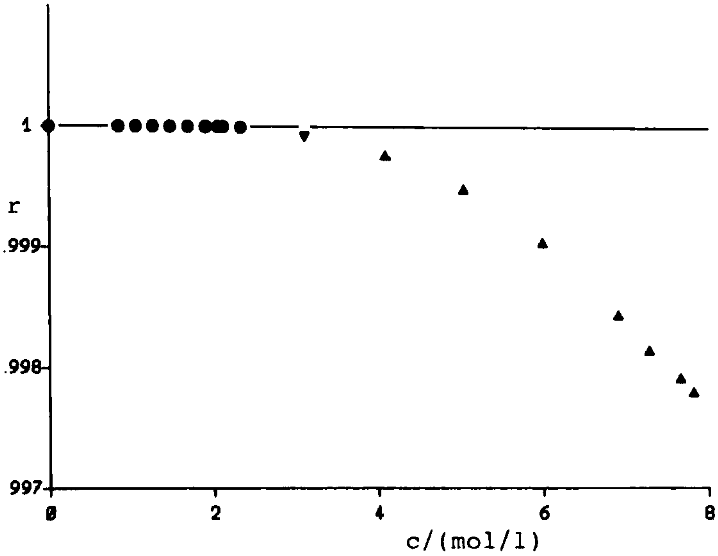

FIG. 4: Correlation factor as a function of the highest concentration in the plot of p vers. ln (c/c* + 1) for region I of carbondioxide at 40.105 and 40.085°C[5].

USE OF THE EQUATIONS FOR ANALYSIS

For the calculation of the concentrations eq. (1) and (2) should be transformed to eq. (5) to (7) which

$$c = c^* \cdot \exp(p/F_p) - c^* \qquad (5) \quad \text{Region I}$$

$$c = c^* \cdot \exp\left(\frac{p - p'}{F_p}\right) - c^* \qquad (6) \quad \text{Region II}$$

$$c = (\ln (p + p^*) - c^o)/F_c \qquad (7) \quad \text{Region III}$$

directly give the concentration c. When a concentration is to be calculated one has to check to which region the pressure measurement corresponds. Then the parameters of the equations are taken from table 1 to 3, for other temperatures interpolated as described, or calculated by use of eq. (3) and (4). With a linear interpolation a sufficient accuracy in most cases is obtained. For other gases the parameters of eq. (1) and (2) can be calculated in the described manner.

EXPERIMENTAL EXAMPLE

The concentration of carbondioxide is to be determined to a given pressure[5] of 46.324 at 75.260°C. The pressure corresponds to region I. The parameters F_p = 133.4 at and c* = 4.59 $mol \cdot l^{-1}$ for this temperature are taken from Table 1. By use of eq. (5) a concentration c of 1.9569 $mol \cdot l^{-1}$ is calculated, whereas the experimental concentration is 1.9567 $mol \cdot l^{-1}$. The error is 10 ppm. The molar concentration can be transferred into density or molar volume in known manner.

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