

Some Physical Properties of Compressed Gases

VI. The Fugacity of Carbon Dioxide

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The Michels' compressibility data for carbon dioxide are smoothed and interpolated by graphical methods, and the fugacity is computed at certain integral pressures. The temperature range is from 0° to 150°C, and the pressure range from 0 to the neighborhood of 3000 atmos. Along all isotherms, the fugacity at first drops below the pressure, the ratio f/p decreasing with p —a phenomenon well known and explained by the attractive forces of the molecules. The minimum in f/p is reached at or near 600 atmos. for all isotherms above critical. With further increase in pressure, the ratio f/p increases, so that the fugacity eventually equals the pressure and thereafter exceeds it. At 50°, $f=p$ at 2435 atmos.; at 150°, $f=p$ at 1675 atmos.

1. THE DATA

THE Michels and their collaborators have published compressibility data and various thermodynamic properties of carbon dioxide.¹⁻³ For facilitating calculations of equilibria involving this gas, it has been thought advisable to add fugacities to the list.

The compressibility data¹⁻³ are published in the form of pv against density and pressure, in isotherms and isochores, the temperature range being from 0° to 150°, and the density range 18.75 to 596 Amagat, i.e., from roughly 0.8 to 27 moles per liter. At 27 moles per liter and 150°C, the pressure is 3240 atmos.

2. A WORD ON AMAGAT UNITS

In order to determine the density of the compressed gas in g/cc, it would be necessary for the experimenter to know not only the volume of the high pressure pipet, but also how many grams of gas there are in it. The custom since the time of Amagat has been to express the densities otherwise, namely, in a unit now called after him, and designating the ratio of the volume that the compressed gas *would* occupy if expanded to 1 atmos. and 0°, to the volume that it actually occupies in the high pressure pipet at pressure p and temperature t °C. Thus, if the Amagat density of a gas at a certain

pressure and temperature is stated to be 20, we know that this same gas would occupy 20 times as much space at 1 atmos. and 0°. Amagat volumes are simply reciprocals of Amagat densities; the Amagat volume of the gas whose density is 20 is therefore 1/20th; i.e., its volume is only 1/20th of what it would be if it were expanded to 1 atmos. and 0°. The Amagat system circumvents the need for weighing the gas; nevertheless, if the density of the gas at 1 atmos. and 0° is known in g/cc from other sources, then it is simple to convert Amagat densities into g/cc, and Amagat volumes into cc/g. Or, if the pv product at some temperature and pressure is known in Amagat units and also in (e.g.) mol. atmos./cc (as is the case at zero pressure and 0°, *vide infra*), then the factor for converting pv and v from the Amagat system into cc atmos./mol. and cc/mol., respectively, is evident.

In practice, the experimental gas is not expanded from the high pressure pipet down to 1 atmos. and 0°, but instead, for convenience, to a pressure only near 1 atmos. and at 25°, wherefore it becomes necessary to translate the measurements at 25° into the standard temperature and pressure (1 atmos., 0°). This translation can be achieved through the following considerations.

Suppose that the relation⁴

$$pv = A + B/v + C/v^2 \quad (36)$$

⁴The equations, figures, and tables are numbered as continuations from those in the previous papers of this series. The references are shown in the next footnote.

¹A. and C. Michels and H. Wouters, Proc. Roy. Soc. A153, 201-224 (1935).

²C. Michels, Thesis (Amsterdam, 1937).

³A. Michels, A. Bijl, and C. Michels, Proc. Roy. Soc. A160, 376-384 (1937).

with the possible addition of a term D/v^4 represents the trend of pv at 25° for low pressure measurements (perhaps to 40 or 50 atmos.) on a certain amount of the gas, v being in any desired units, such as cc. Also, let a similar series with constants A_0, B_0, C_0 represent the trend at 0°. A and A_0 , it will be noticed, are the pv products at infinite attenuation ($p=\rho=0$), hence if v_1 denotes the volume of the gas at 0° and 1 atmos., then the ratio $1+\lambda$ of the pv product at 0° and infinite attenuation to the pv product at 0° and 1 atmos. will be

$$1+\lambda = 1/(1+B_0/A_0v_1+C_0/A_0v_1^2), \quad (37)$$

where

$$v_1 = A_0 + B_0/v_1 + C_0/v_1^2. \quad (38)$$

Evidently $1+\lambda$ is the value of pv in Amagat units for 0° and infinite attenuation; it is independent of the amount of gas used, and of the units in which v is measured.

Now since at infinite attenuation, the pv product for a given mass of gas is proportional to the absolute temperature, we may write

$$(pv)_s = (pv)_{25} \frac{T_0}{T_0+25} \times \frac{1}{(1+B/Av+C/Av^2)_{25}} \frac{1}{1+\lambda} \quad (39)$$

for the relation between the pv product of a given mass of the gas at 25° and some low pressure usually near 1 atmos., and the pv product of the same gas under standard conditions (0° and 1 atmos., denoted by the subscript s). T_0 denotes the ice point, which, following the Michels, we assume in this work to be 273.15°C.

In practice the gas is expanded from the high pressure pipet at pressure p and temperature t into a calibrated low pressure pipet at 25° (usually near 1 atmos.), whereupon $(pv)_{25}$ is determined; thence by the relation just written comes also $(pv)_s$, which is numerically the volume that this same gas would occupy under standard conditions; the ratio of the volume occupied at the high pressure p and temperature t to that which it would occupy under standard conditions is the required Amagat volume v at the high pressure p and temperature t . The

product of p and v gives the recorded pv in Amagat units corresponding to p and t .

It is worthy of note that though A_0, B_0 , and C_0 all appear in the expression for $1+\lambda$ (Eq. 37), they do so only through the small correction term B_0/A_0 and the still smaller one C_0/A_0 ; hence $1+\lambda$ is determined with much greater relative precision than any of the parameters A_0, B_0 , and C_0 . In this work on carbon dioxide we found from the seven low pressure points at 0° cited in the first footnote,

$$1+\lambda = 1.00679,$$

the root mean square variation being 0.00005 in the seven residuals, there being 7-3 degrees of freedom. The Michels used 1.006824, which is not significantly different.

Similar remarks hold for the precision of the denominator of Eq. (39), wherein A, B , and C for 25° also enter only as correction terms. It follows that with reasonably good compressibility data along the 0° and 25° isotherms, there should be negligible error in translating $(pv)_{25}$ into $(pv)_s$, and the units of pv should therefore be dependably Amagat.

3. SOME CONVERSION FACTORS FOR CARBON DIOXIDE

Birge's value 22414.1 ± 0.8 cc for the volume of a mol. of a perfect gas at 1 atmos. and 0° seems well established. The atomic weight of carbon is not so certain, but we adopt 12.010 which is more than close enough for any conversions that may be needed. With our value of $1+\lambda$ (*vide supra*) we can then say that

At $t=0^\circ, p=0$,

$$pv = RT_0 = 22414.1 \text{ cc atmos./mol. (Birge)}$$

$$pv = 1+\lambda = 1.00679 \text{ Amagat units}$$

$$pv = 509.30 \text{ cc atmos./g}$$

At $t=0^\circ, p=1, pv=1$ in Amagat units (definition)

$$pv = 22414.1/(1+\lambda) = 22263.0 \text{ cc atmos./mol.}$$

$$pv = 22263/44.010 = 505.86 \text{ cc atmos./g}$$

$$pv = 22.4141/1000.03(1+\lambda)$$

$$= 22.2623 \text{ l atmos./mol.}$$

By obvious divisions it follows that to convert (i) Amagat densities into mol./cc, divide them by 22263.0, or multiply them by 0.0000449177.

TABLE VI. The fugacity of carbon dioxide at integral pressures. * denotes extrapolation; (s) saturation.

p ATMOS.	ρ MOL./LITER	LOG f/p	f ATMOS.	p ATMOS.	ρ MOL./LITER	LOG f/p	f ATMOS.
$t=0^\circ$				$t=32^\circ$ —(Continued)			
1	0.044919	$\bar{1}.99684$	0.99275	700	24.2	0.349	157
25	1.39	.9211	20.8	800	24.7	.361	184
34.12(s)	2.19	.8882	26.4	900	25.2	.377	214
$t=5^\circ$				1000	25.5	.398	250
1	.044094	$\bar{1}.99707$	0.99328	1500	27.0	.552	535
25	1.34	.9266	21.1	$t=40^\circ$			
38.30(s)	2.50	.8807	29.1	1	.039085	$\bar{1}.99816$	0.99577
$t=10^\circ$				25	1.10	.954	22.5
1	.043300	$\bar{1}.99724$	0.99367	50	2.62	.904	40.1
25	1.30	.9308	21.3	75	5.46	.837	51.5
44.32(s)	3.05	.8675	32.7	100	14.4	.764	58.1
$t=15^\circ$				150	17.8	.639	65.3
1	.042534	$\bar{1}.99741$	0.99405	200	19.1	.561	72.8
25	1.26	.9352	21.5	300	20.8	.469	88.3
50	3.60	.8580	36.1	400	21.8	.431	108
50.50(s)	3.69	.8561	36.3	500	22.6	.409	128
$t=20^\circ$				600	23.3	.402	151
1	.041796	$\bar{1}.99754$	0.99435	700	23.9	.405	178
25	1.22	.9385	21.7	800	24.5	.417	209
50	3.28	.8579	36.0	900	25.0	.433	244
56.59(s)	4.43	.8454	39.6	1000	25.4	.454	284
$t=25^\circ$				1500	26.9	.593	588
1	.041083	$\bar{1}.99770$	0.99472	$t=50^\circ$			
25	1.19	.9425	21.9	1	.037860	$\bar{1}.99828$.99605
50	3.05	.8770	37.7	25	1.05	.957	22.7
63.47(s)	5.50	.8343	43.3	50	2.43	.910	40.6
$t=30^\circ$				75	4.52	.858	54.1
1	.040394	$\bar{1}.99792$	0.99522	100	9.13	.798	62.8
25	1.16	.9480	22.2	150	16.1	.675	71.1
50	2.88	.8860	38.5	200	17.9	.601	79.8
71.16(s)	7.75	.8155	46.5	300	19.8	.516	98.4
$t=31.04^\circ$				400	21.1	.471	118
1	0.040263	$\bar{1}.99784$	0.99504	500	22.1	.452	142
25	1.15	.946	22.1	600	22.8	.450	169
50	2.86	.886	38.5	700	23.4	.454	199
75	14.6	.810	48.4	800	23.8	.462	232
100	17.4	.712	51.5	900	24.2	.478	271
150	19.0	.573	56.1	1000	24.6	.497	314
200	20.1	.498	63.0	1500	26.2	.641	657
300	21.0	.414	77.8	*2000	27.6	.825	1337
400	22.2	.372	94.2	$t=75^\circ$			
500	23.1	.348	111	1	.035111	$\bar{1}.99864$	0.99688
600	23.7	.336	130	25	0.950	.966	23.1
700	24.3	.335	151	50	2.09	.931	42.7
800	24.7	.343	176	75	3.53	.895	58.9
900	25.1	.357	205	100	5.43	.858	72.1
1000	25.5	.379	239	150	10.9	.782	90.8
*1500	27.1	.549	531	200	14.6	.717	104
$t=32^\circ$				300	17.7	.631	128
1	.040126	$\bar{1}.99788$	0.99513	400	18.9	.592	156
25	1.14	.947	22.1	500	20.2	.572	187
50	2.82	.890	38.8	600	21.2	.567	222
75	12.7	.816	49.1	700	22.0	.573	262
100	17.1	.720	52.5	800	22.6	.585	308
150	19.0	.578	56.8	900	23.1	.600	358
200	20.1	.495	62.6	1000	23.6	.619	416
300	21.3	.416	78.2	1500	25.3	.745	835
400	22.2	.375	94.9	2000	26.7	.909	1622
500	23.1	.353	113	*2500	27.6	0.082	3019
600	23.6	.345	133	$t=100^\circ$			
$t=32^\circ$				1	.032969	$\bar{1}.99900$	0.99770
1	.040126	$\bar{1}.99788$	0.99513	25	0.870	.975	23.6
25	1.14	.947	22.1	50	1.86	.947	44.3
50	2.82	.890	38.8	75	3.01	.921	62.5
75	12.7	.816	49.1	$t=100^\circ$			
100	17.1	.720	52.5	1	.032969	$\bar{1}.99900$	0.99770
150	19.0	.578	56.8	25	0.870	.975	23.6
200	20.1	.495	62.6	50	1.86	.947	44.3
300	21.3	.416	78.2	75	3.01	.921	62.5
400	22.2	.375	94.9	$t=100^\circ$			
500	23.1	.353	113	1	.032969	$\bar{1}.99900$	0.99770
600	23.6	.345	133	25	0.870	.975	23.6

TABLE VI.—Continued.

p ATMOS.	ρ MOL./LITER	LOG f/p	f ATMOS.	p ATMOS.	ρ MOL./LITER	LOG f/p	f ATMOS.
$t=100^\circ$ —(Continued)				$t=125^\circ$ —(Continued)			
100	4.37	0.894	78.3	800	20.0	0.749	449
150	7.69	.839	104	900	20.8	.763	521
200	11.1	.790	123	1000	21.4	.777	599
300	15.2	.721	158	1500	23.6	.887	1156
400	17.3	.683	193	2000	25.0	0.0275	2131
500	18.7	.664	231	2500	26.2	.180	3784
600	19.8	.658	273	*3000	27.2	.338	6533
700	20.6	.662	321	$t=150^\circ$			
800	21.3	.674	378	1	.028843	1.99932	0.99844
900	21.9	.691	442	25	0.748	.983	24.0
1000	22.4	.710	513	50	1.55	.967	46.4
1500	24.4	.831	1018	75	2.42	.951	67.0
2000	25.9	.987	1941	100	3.36	.936	86.3
2500	27.0	0.1625	3634	150	5.39	.906	121
$t=125^\circ$				200	7.54	.879	151
1	.030667	1.99920	0.99816	300	11.3	.835	205
25	0.803	.980	23.9	400	13.9	.809	258
50	1.69	.959	45.5	500	15.7	.797	314
75	2.67	.938	65.0	600	17.0	.795	374
100	3.77	.918	82.8	700	18.1	.798	440
150	6.26	.880	114	800	19.0	.806	512
200	8.91	.843	139	900	19.8	.820	595
300	13.1	.786	183	1000	20.4	.838	689
400	15.5	.754	227	1500	22.7	.952	1345
500	17.1	.737	273	2000	24.4	0.0965	2498
600	18.3	.734	326	2500	25.6	.253	4476
700	19.3	.740	385	3000	26.7	.414	7783

(ii) Amagat densities into g/cc, divide them by 505.86, or multiply them by 0.0019768.
 (iii) Amagat densities into mol./l, divide them by 22.2623, or multiply them by 0.0449189.

4. THE PROCEDURE

In our previous work,⁵ which had involved gases at temperatures considerably above their critical temperatures, we had smoothed and differentiated the data by means of large scale graphs of Δ and α plotted in isobars and isotherms against suitable functions of temperature or pressure. Δ was defined as $v(pv/RT-1)$ and α as $v(RT/pv-1)$. For the data on carbon dioxide, however, a deviation function of different behavior was desired: after some trials, the function

$$\sigma = Tv \log pv/RT, \quad (40)$$

being one of several suggested to us by Mr. C. S. Cragoe of the National Bureau of Standards,

⁵ W. Edwards Deming and Lola E. Shupe, I (nitrogen) Phys. Rev. 37, 638-654 (1931); II (carbon monoxide) 38, 2245-2264 (1931); III (hydrogen) 40, 848-859 (1932); IV (entropies) 45, 109-113; V (nitrogen) 48, 448-9 (1935).

was found to be satisfactory. Like the previous Δ and α , so also σ measures the departure from the perfect gas law, and magnifies the experimental irregularities, especially at low pressures.

The data presented by Michels are in uneven temperatures, e.g. 25.053°, 31.037°, ..., 75.260°, etc. Smoothing and reduction to integral temperatures and pressures was accomplished by drawing large scale plots of σ , one chart showing σ in isochores against t , another showing σ in isotherms against the density, ρ . These curves, after adjustment, represent traces of a σ , ρ , t surface. To obtain therefrom traces of the same surface at integral temperatures, values of σ were read from the smoothed isochores of σ vs. t at the desired integral temperatures (see Table VI). Having a smoothed value of σ at any chosen temperature and density, one can compute the corresponding pressure from the definition of σ , namely $Tv \log pv/RT$.

To find the densities at the integral pressures in Table VI, a chart was made showing σ vs. p in isotherms; σ read therefrom at any desired integral pressure establishes the corresponding

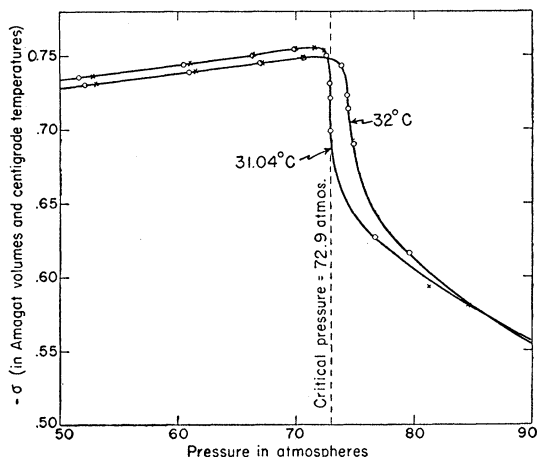


FIG. 29. Isotherms showing σ vs. p at 31.04° and 32° in the neighborhood of the critical region. The crosses are experimental points. The circles are interpolated from the σ vs. ρ isotherms (not shown) for assistance in drawing the curves. The σ vs. ρ isotherms exhibit no peculiarities in this region, being perfectly regular.

density (ρ or $1/v$) through the equation

$$\sigma = Tv \log pv/RT.$$

The σ vs. p isotherm at the critical temperature (31.04°C as given by Michels) exhibits a discontinuous slope at the critical pressure, as is seen in Fig. 29: this follows from the fact that at the critical point $(dp/dv)_T = 0$, wherefore $(d\sigma/dp)_T = \infty$. The vertical part of the 31.04° isotherm points to 72.9 atmos. as the critical pressure. The Michels give 72.85 atmos., which is in good agreement. Actually, a steep slope occurs also at temperatures just above the critical, as is seen in the isotherm for 32° in Fig. 29.

Fugacities were computed by graphical integrations according to the equation

$$\log f/p = -(0.4343/RT) \int_0^p \alpha dp, \quad (28)$$

wherein $\alpha = v(RT/pv - 1)$, as previously defined. In place of graphical integrations, two terms of

the Euler-Maclaurin summation

$$\int_1^{p_2} \alpha dp = \frac{1}{2}(\alpha_1 + \alpha_2)(p_2 - p_1) - \frac{1}{12}(p_2 - p_1)^2 \left[\frac{d\alpha}{dp} \right]_1 + \dots \quad (41)$$

were useful when the α vs. p isotherms did not have high curvature. At high densities the integral in Eq. (41) was conveniently evaluated as $\int (\alpha v^2 dp/dv)_T dv$, for the reason that in this region the density scale is much compressed relative to the pressure scale.

5. THE RESULTS

The results are shown in Table VI. The calculations are considered to be consistent with the experimental data to as many figures as written. Extrapolations (never very long) are starred. Below the critical temperature the calculations are carried up to the saturation densities (marked by an *s* in the table), these points having been determined from the work of Myers and Van Dusen⁶ on the vapor pressure of carbon dioxide.

The interpolation of fugacities for any intermediate argument (density, temperature, or pressure) is accomplished easier with $\log f/p$ than with f itself, and this is the reason for showing $\log f/p$. Moreover, the graphs of $\log f/p$ against p are nearly linear to 50 atmos.; then since $f=0$ and $\log f/p=0$ at $p=\rho=0$, if one wished to know the fugacity (e.g.) at 3 atmos. and 40°, he would interpolate by proportional parts between $p=0$ and $p=25$, finding $\log f/p = (3/25)(\bar{1}.954) = \bar{1}.99448$, whence $f/p = 0.98737$, and $f = 3 \times 0.98737 = 2.962$ atmos.

In conclusion it is a pleasure to mention the helpful interest of our friends Mr. C. S. Cragoe of the National Bureau of Standards, and Drs. A. and C. Michels in Amsterdam.

⁶ C. H. Myers and M. S. Van Dusen, Nat. Bur. Stand. J. Research **10**, 381-412 (1933).