

## Some Physical Properties of Compressed Gases. IV. The Entropies of Nitrogen, Carbon Monoxide and Hydrogen

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Previous work on these gases has yielded values for the expansion coefficients  $(T/v)(dv/dT)_p$ ,  $-(p/v)(dv/dp)_T$ , and for  $-T(d^2v/dT^2)_p$  at temperatures between  $-70^\circ$  and  $400^\circ$  or  $500^\circ\text{C}$  and at pressures between 25 and 1200 atmospheres. The evaluation of such derivatives renders possible the calculation of many physical properties of the substance. To those properties that have been reported previously for nitrogen, carbon monoxide and hydrogen, the authors now add the change in entropy  $\Delta S = -\int_1^p (dv/dT)_p d\ln p$  along isotherms. The integral is evaluated by graphical quadrature from the previously determined expansion coefficient  $(T/v)(dv/dT)_p$ . The absolute entropy at various pressures along an isotherm is then obtained by adding  $\Delta S$  to the entropy at one atmosphere. The calculated values of  $\Delta S$  are shown in a table, and the absolute entropies are shown by isotherms at various temperatures between  $-75^\circ$  and  $600^\circ\text{C}$  to 1200 atmospheres. With an ideal gas, the integral  $\Delta S = -\int_1^p (dv/dT)_p d\ln p$  would be simply  $-R \ln p$  along all isotherms. The authors' calculations show that  $\Delta S$  is always greater in absolute value than  $R \ln p$ , the difference being more pronounced at low

temperatures and high pressures as would be expected. At 1200 atmospheres and at ordinary temperatures, all three gases have lost roughly 15 units of entropy. When an actual gas is compressed along an isotherm,  $(dv/dT)_p$  has at first the value that it would have if the gas were ideal, namely,  $R/p$ , but it gradually becomes greater than  $R/p$ . This disparity continues until with sufficient pressure a point is reached where  $(dv/dT)_p$  again becomes equal to, and finally less than,  $R/p$ . Eventually  $(dv/dT)_p$  must become so small that  $|p^c(dv/dT)_p|$  with  $c > 1$  remains bounded, in order that  $\Delta S$  may be finite when  $p$  is infinite. The authors find that  $(dv/dT)_p$  for these gases becomes equal to  $R/p$  at about 1200 atmospheres. If  $(dv/dT)_p \neq R/p$  and  $p > 1000$ , the pressure must be raised to  $2 \times 10^6$  atmospheres or higher to extract an additional 15 units of entropy. Hence it would seem impossible ever to reduce one of these gases above the critical temperature to a state of near zero entropy by the application of pressure alone, unless the graph of  $(dv/dT)_p$  against  $p$  has humps or infinite discontinuities (giving convergent integrals) beyond 1000 atmospheres.

THE authors' graphical method for evaluating the derivatives  $(T/v)(dv/dT)_p$ ,  $-(p/v)(dv/dp)_T$ , and  $-T(d^2v/dT^2)_p$  from  $p$ ,  $v$ ,  $T$  data of gases has made possible the calculation of a number of physical properties. This method is especially applicable when the  $p$ ,  $v$ ,  $T$  data are taken at a large number of points in the temperature and pressure ranges covered, as fortunately happens to be the case with the compressibility work done by Bartlett and his co-workers at this laboratory. Calculations of density, temperature and pressure expansion coefficients, heat capacities at constant volume and constant pressure, fugacity and the Joule-Thomson coefficient have been published for nitrogen,<sup>1</sup> carbon monoxide<sup>2</sup> and hydrogen.<sup>3</sup> At the sug-

gestion of our colleague Dr. Oliver R. Wulf, we have now included entropy in the calculations, and we wish at this time to present the results for the three gases just named.

With the temperature coefficient  $(T/v)(dv/dT)_p$  already computed it is a simple matter to evaluate

$$\Delta S = -\int_1^p (dv/dT)_p d\ln p \quad (31)^*$$

graphically along isotherms, except at the low pressure end below 50 atmospheres where the steepness and curvature of the plots of  $(dv/dT)_p$  against  $p$  rendered the work difficult and inexact. The integrations from 1 to 25 and from 1 to 50 atmospheres were accordingly performed analytically by the following procedure.

<sup>1</sup> W. Edwards Deming and Lola E. Shupe, *Phys. Rev.* **37**, 638 (1931).

<sup>2</sup> W. Edwards Deming and Lola E. Shupe, *Phys. Rev.* **38**, 2245 (1931).

<sup>3</sup> W. Edwards Deming and Lola E. Shupe, *Phys. Rev.* **40**, 848 (1932).

\* The equations, figures and tables in this article will be numbered as continuations from the previous ones.

The integrand can be written as the product of the two factors  $v/T$  and  $(T/v)(dv/dT)_p$ , and both of these factors can be expressed by a series in  $p$ . Examination of the published Tables I, II and III suggests that the expansion coefficients can probably be well represented along isotherms by the series

$$\begin{aligned}(T/v)(dv/dT)_p &= 1 + a'p + b'p^2, \\ - (p/v)(dv/dp)_T &= 1 + ap + bp^2,\end{aligned}$$

up to about 100 atmospheres. The adjustable

parameters in these series were determined by fitting them to the published values of the expansion coefficients along each isotherm. All four parameters would of course be zero if the gas were ideal.

By integration of the second series with the condition that  $pv = RT$  at  $p=0$ , it is easy to deduce that

$$\begin{aligned}v &= (RT/p)e^{-(ap + \frac{1}{2}bp^2)} \\ &\doteq (RT/p)[1 - ap + \frac{1}{2}(a^2 - b)p^2]\end{aligned}$$

closely enough. Thence

$$\begin{aligned}\Delta S &= - \int_1^p (dv/dT)_p dp = - (1/T) \int_1^p v(T/v)(dv/dT)_p dp \\ &= - (1/T) \int_1^p (RT/p)[1 - ap + \frac{1}{2}(a^2 - b)p^2][1 + a'p + b'p^2] dp \\ &= - R[\ln p/1 + (a' - a)(p - 1) + \frac{1}{2}(b' - aa' + \frac{1}{2}a^2 - \frac{1}{2}b)(p^2 - 1^2)].\end{aligned}$$

In this manner the integrations along isotherms were performed up to 25, 50 and 75 atmospheres. The last limit was included to permit comparison of the analytical and graphical methods in the vicinity of 50 atmospheres, and to tie together the results of the upper and lower ranges.

In this paper we have used  $R = 1.9869$  cal./mol·deg. as given by the I.C.T., so that our values with Johnston's (*vide infra*) will form a consistent set. The values of  $\Delta S$  are shown in Table IV. The hydrogen is probably closely a 3 : 1 orthopara mixture at all the temperatures and pressures in Bartlett's compressibility work.

There seems to be no reliable way of estimating the probable errors of the entries in Table IV. Below 100 atmospheres and above  $-25^\circ\text{C}$ , we venture to suggest 0.02 cal./mol·deg. as a conservative estimate of the probable error in  $\Delta S$ . At lower temperatures and higher pressures the precision will be less. At 1000 atmospheres the probable error may be as high as 0.1. Values listed above 1000 atmospheres, and those above  $400^\circ\text{C}$  and below  $-70^\circ\text{C}$ , were obtained by extrapolating  $p$ ,  $v$ ,  $T$  data on suitable charts, and may therefore have still lower precision. These estimates of probable errors apply as well to the absolute entropies obtained by adding  $\Delta S$

to the absolute entropy at 1 atmosphere (*vide infra*), since values of the latter are subject to practically no experimental error. However, *relative* changes in entropy, obtained by subtracting one value from another not far removed on the same isotherm should be fairly exact, and for this reason two decimals are listed throughout Table IV.

To get absolute entropies,  $\Delta S$  must be added to  $S'$ , the entropy of the *actual* gas at one atmosphere. Absolute entropies at one atmosphere calculated from spectroscopic data are for the gas in the *ideal* state, and it is necessary to make proper correction. The difference between the entropy of the gas in the actual state and the entropy of the same gas in the ideal state is

$$\begin{aligned}S_{\text{act}} - S_{\text{ideal}} &= - \int_0^p \{(dv/dT) - (dv/dT)_{\text{id}}\} dp \\ &= - \int_0^p \{(dv/dT) - RT/p\} dp \\ &= - \int_0^p \{(dv/dT) - v/T - \alpha/T\} dp \\ &= - (1/T) \int_0^p \mu C_p dp + (1/T) \int_0^p \alpha dp,\end{aligned}\tag{32}$$

TABLE IV. *The decrease in the entropies of nitrogen, carbon monoxide and hydrogen along isotherms, from their entropies at one atmosphere. The units are calories per mol per degree.*

<i>t</i> °C	Gas	Pressure in Atmospheres													
		25	50	75	100	150	200	300	400	500	600	800	1000	1100	1200
-75	H <sub>2</sub>	6.43	7.84	8.69	9.28	10.14	10.75	11.63	12.25	12.73	13.13	13.74	14.21	14.41	14.59
-70	CO	6.67	8.32	9.44	10.31	11.61	12.51	13.65	14.31	14.81	15.24	15.89	16.40	16.62	16.81
	N <sub>2</sub>	6.65	8.38	9.48	10.34	11.60	12.46	13.52	14.22	14.73	15.14	15.77	16.27	16.47	16.65
-50	H <sub>2</sub>	6.42	7.82	8.66	9.25	10.10	10.70	11.56	12.17	12.66	13.05	13.66	14.12	14.32	14.49
	CO	6.65	8.18	9.24	10.04	11.23	12.07	13.17	13.87	14.39	14.80	15.46	15.96	16.17	16.36
	N <sub>2</sub>	6.62	8.26	9.31	10.10	11.31	12.17	13.25	13.95	14.47	14.88	15.52	16.03	16.24	16.42
-25	H <sub>2</sub>	6.42	7.81	8.64	9.23	10.05	10.65	11.49	12.10	12.57	12.95	13.56	14.02	14.22	14.39
	CO	6.59	8.12	9.11	9.87	10.96	11.75	12.82	13.54	14.07	14.48	15.14	15.64	15.85	16.04
	N <sub>2</sub>	6.58	8.21	9.19	9.92	11.03	11.82	12.89	13.60	14.13	14.54	15.20	15.70	15.91	16.11
0	H <sub>2</sub>	6.41	7.80	8.63	9.21	10.04	10.63	11.47	12.08	12.54	12.92	13.52	13.98	14.18	14.36
	CO	6.55	8.03	8.99	9.70	10.74	11.50	12.54	13.25	13.80	14.22	14.88	15.36	15.57	15.76
	N <sub>2</sub>	6.53	8.14	9.08	9.78	10.82	11.57	12.63	13.35	13.89	14.32	14.98	15.49	15.71	15.91
20	N <sub>2</sub>	6.51	8.02	8.94	9.62	10.62	11.37	12.40	13.12	13.66	14.10	14.76	15.28	15.50	15.71
25	H <sub>2</sub>	6.41	7.77	8.60	9.19	10.02	10.62	11.46	12.06	12.53	12.91	13.50	13.96	14.16	14.33
	CO	6.53	7.98	8.92	9.60	10.61	11.34	12.38	13.09	13.63	14.06	14.71	15.21	15.42	15.62
50	H <sub>2</sub>	6.41	7.79	8.60	9.18	10.01	10.60	11.43	12.03	12.49	12.86	13.45	13.91	14.10	14.27
	CO	6.51	7.94	8.85	9.52	10.51	11.22	12.22	12.94	13.48	13.91	14.57	15.07	15.29	15.48
	N <sub>2</sub>	6.48	7.97	8.86	9.52	10.48	11.18	12.19	12.91	13.45	13.89	14.56	15.08	15.31	15.57
100	H <sub>2</sub>	6.40	7.79	8.60	9.18	10.01	10.59	11.41	12.00	12.46	12.84	13.42	13.87	14.07	14.24
	CO	6.48	7.87	8.76	9.40	10.34	11.03	12.01	12.71	13.25	13.68	14.34	14.86	15.08	15.27
	N <sub>2</sub>	6.46	7.91	8.77	9.40	10.32	10.99	11.94	12.64	13.17	13.61	14.28	14.81	15.03	15.24
150	CO	6.46	7.89	8.77	9.40	10.31	10.97	11.93	12.62	13.15	13.58	14.26	14.79	15.01	15.20
200	H <sub>2</sub>	6.40	7.79	8.61	9.18	10.00	10.57	11.39	11.98	12.43	12.80	13.38	13.83	14.02	14.20
	CO	6.45	7.85	8.71	9.33	10.22	10.87	11.81	12.50	13.02	13.46	14.14	14.67	14.89	15.09
	N <sub>2</sub>	6.44	7.90	8.74	9.35	10.22	10.85	11.75	12.40	12.91	13.33	13.98	14.49	14.70	14.90
300	H <sub>2</sub>	6.40	7.78	8.59	9.17	9.98	10.55	11.36	11.95	12.40	12.77	13.35	13.79	13.99	14.16
	CO	6.43	7.81	8.65	9.26	10.13	10.76	11.67	12.32	12.84	13.26	13.92	14.44	14.66	14.86
	N <sub>2</sub>	6.42	7.86	8.68	9.28	10.12	10.73	11.59	12.21	12.69	13.09	13.72	14.20	14.41	14.60
400	H <sub>2</sub>	6.40	7.77	8.58	9.16	9.96	10.54	11.35	11.93	12.38	12.75	13.32	13.77	13.96	14.14
	CO	6.42	7.77	8.60	9.19	10.04	10.65	11.53	12.17	12.68	13.09	13.75	14.27	14.48	14.68
	N <sub>2</sub>	6.40	7.80	8.62	9.21	10.05	10.64	11.49	12.09	12.56	12.95	13.56	14.04	14.24	14.43
500	H <sub>2</sub>	6.40	7.76	8.58	9.16	9.96	10.54	11.35	11.93	12.38	12.75	13.32	13.77	13.96	14.14
	N <sub>2</sub>	6.40	7.82	8.63	9.21	10.03	10.61	11.45	12.05	12.51	12.89	13.50	13.97	14.17	14.36
600	N <sub>2</sub>	6.40	7.82	8.64	9.22	10.04	10.62	11.44	12.03	12.49	12.87	13.47	13.94	14.14	14.32
		<i>For Comparison</i>													
	Ideal	6.40	7.77	8.58	9.15	9.96	10.53	11.33	11.90	12.35	12.71	13.28	13.73	13.91	14.09

where  $\alpha = RT/p - v = -v(RT/pv - 1)$ , and  $\mu$  and  $C_p$  denote the Joule-Thomson coefficient and the heat capacity at constant pressure. The derivatives ( $dv/dT$ ) are understood to be taken at constant pressure, and refer to the actual gas unless written with the subscript "*id.*" If the upper limit is one atmosphere the integrands may be considered constant over the interval of integration, so at one atmosphere the last

equation gives

$$S' - S^\circ = -\mu C_p / T + \alpha / T, \quad (33)$$

wherein  $\mu C_p$  and  $\alpha$  are to be evaluated anywhere in the neighborhood of zero pressure. This can be done by means of the tables already published, remembering that  $-\alpha$  at  $p=0$  is the second virial coefficient. The corrections  $S' - S^\circ$  vary

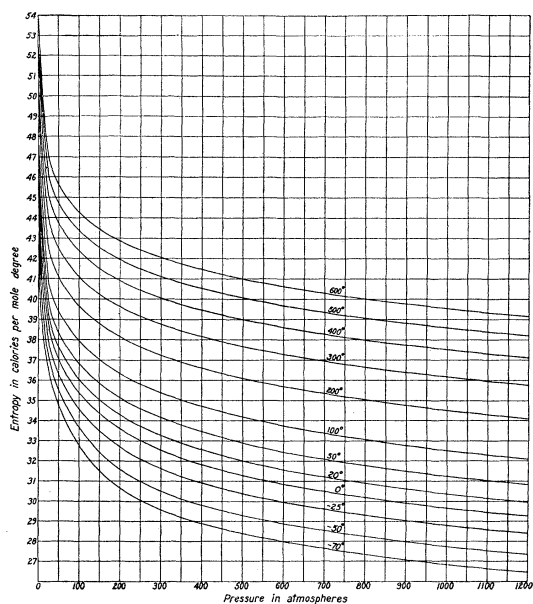


FIG. 25. The entropy of nitrogen along various isotherms as a function of pressure.

from negligible amounts up to several hundredths cal./mol. deg., as shown in Table V.

The values of  $S^\circ$  were kindly furnished by Professor H. L. Johnston and Mr. C. O. Davis of Ohio State University, who interpolated their data for us in advance of publication.<sup>4</sup>

The values of  $S$  found by adding  $\Delta S$  to  $S'$  are shown by the isotherms of Figs. 25, 26 and 27.

TABLE V. The absolute entropy  $S^\circ$  of ideal hydrogen, carbon monoxide and nitrogen at one atmosphere, furnished by H. L. Johnston and C. O. Davis.

The difference  $S' - S^\circ$  between the entropy of the ideal gas and the actual gas at one atmosphere  $S' - S^\circ = \mu C_p/T - \alpha/T$ . The units are calories per mol per degree.  $\mu C_p$  and  $\alpha$  are found from previous publications, see footnotes 1, 2, 3. Nuclear spin excluded.

$t$ °C	Hydrogen (3:1)		Carbon Monoxide		Nitrogen	
	$S^\circ$	$S' - S^\circ$	$S^\circ$	$S' - S^\circ$	$S^\circ$	$S' - S^\circ$
-75	28.474	-0.008	44.643	0.005	43.118	-0.019
-70						
-50	29.257	.008	45.296	.002	43.770	-.016
-25	29.970	.019	46.035	.000	44.507	-.013
0	30.624	.024	46.703	-.002	45.176	-.010
25	31.225	.027	47.313	-.003	45.786	-.007
50	31.782	.029	47.874	-.005	46.346	-.006
100	32.784	.059	48.878	-.005	47.352	-.004
150			49.760	-.006		
200	34.437	.027	50.549	-.006	49.012	-.002
300	35.779	.024	51.921	-.006	50.368	-.001
400	36.914	.022	53.097	-.006	51.536	.000
500	37.883	.020			52.559	.000
600					53.477	.000

<sup>4</sup> H. L. Johnston and C. O. Davis, J. Am. Chem. Soc., to appear.

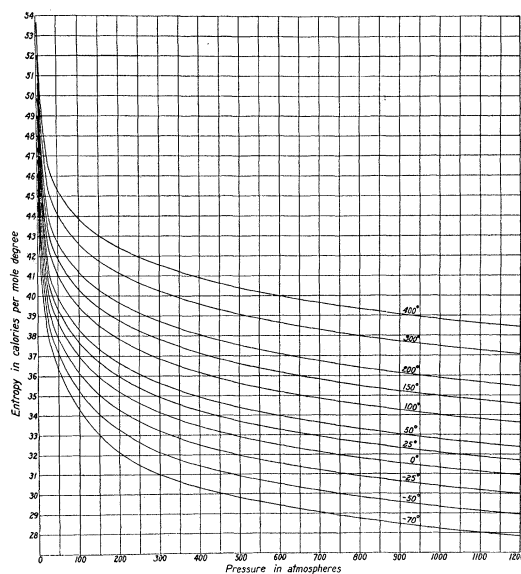


FIG. 26. The entropy of carbon monoxide along various isotherms as a function of pressure.

#### DISCUSSION

If the gas were ideal, the values of  $-\Delta S$  would be merely  $R \ln p$  at all temperatures. Values of  $R \ln p$  are shown at the bottom of Table IV for comparison with the values of  $-\Delta S$  obtained for the actual gases. It will be noticed that the decrease in entropy of the actual gases

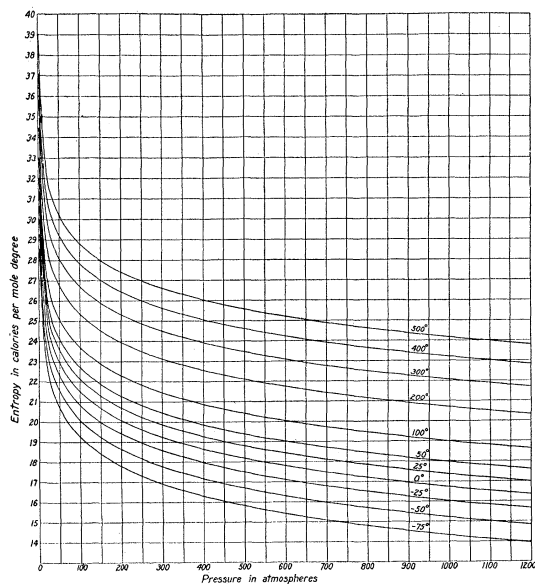


FIG. 27. The entropy of hydrogen along various isotherms as a function of pressure.

is in all cases greater than it would be for the ideal gas. This is to be expected at moderate pressures, for according to van der Waals' equation

$$(p + a/v^2)(v - b) = RT$$

we should have

$$(dv/dT)_p = R/(p - a/v^2 + 2ab/v^3) > R/p \quad (34)$$

and consequently

$$\begin{aligned} -\Delta S &= \int_1^p (dv/dT)_p dp \\ &= R \int_1^p (p - a/v^2 + 2ab/v^3)^{-1} dp > R \ln p. \quad (35) \end{aligned}$$

This integral is divergent, as is easiest seen by transforming  $(p - a/v^2 + 2ab/v^3)^{-1} dp$  into  $d \ln (v - b)$ . But if a substance be subjected to an ever increasing pressure at any temperature, its entropy must decrease to zero or possibly some finite amount,<sup>5</sup> so the integral for  $\Delta S$  must be convergent and not divergent. Consequently van der Waals' equation must sooner or later break down. Indeed, for any actual gas, the integrand  $(dv/dT)_p$  must at some pressure become and

remain less than  $R/p$ , and in such a manner that

$$|p^c (dv/dT)_p| \text{ with } c > 1$$

remains bounded, if the integral for  $\Delta S$  is to be convergent.

Differences of  $\Delta S$  from one pressure to another in Table IV indicate that for all three gases the integrand  $(dv/dT)_p$  becomes equal to  $R/p$  at about 1200 atmospheres for all the isotherms here studied, because the changes in  $\Delta S$  that accompany changes in pressure from 1000 to 1100 and from 1100 to 1200 atmospheres are about the same as those of the ideal gas.

If a substance had the same value of  $(dv/dT)_p$  as the ideal gas, namely  $R/p$ , a change of pressure from 1000 to  $2 \times 10^6$  atmospheres would be required to extract 15 more units of entropy. Hence, it would seem that if one of these gases is to be reduced to a state of zero entropy by the application of pressure, there must be humps or infinite discontinuities (giving convergent integrals) in the graph of  $(dv/dT)_p$  against  $p$ , somewhere above 1000 atmospheres.

In conclusion the authors wish to express their indebtedness to Dr. Oliver R. Wulf for suggesting these calculations and for his continued interest and help. Professor H. L. Johnston and Mr. C. O. Davis furnished the values of  $S^\circ$ .

<sup>5</sup> G. N. Lewis, *Zeits. f. physik. Chemie* **130**, 532 (1927).