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Gas Imperfections Determined from the Heat of Vaporization and Vapor Pressure

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The imperfections of many gases may be obtained by combining available heats of vaporization and vapor pressure data with the Clausius-Clapeyron equation. The accuracy of this method in some cases is comparable to that of good direct P.V.T. measurements and therefore may be useful in preliminary investigations. If P is the vapor pressure, T is the absolute temperature, ΔH is the heat of vaporization, V and V_l are the molal volumes of the vapor and liquid phases:

$$\frac{PV}{RT} = \frac{-\Delta H}{R(1 - V_l/V)[d \ln P/d(1/T)]} = 1 + \beta.$$

This equation determines the gas imperfection β . The value

of β calculated in this manner is compared with experimental second virial coefficients for H_2O , NH_3 , H_2 , O_2 , A , CH_4 , propane, n -butane, n -heptane, ethene, propene, CH_2Cl , CCl_3F , CH_3OH , C_6H_6 , and Hg . Values of β are determined for HI , HBr , HCl , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, HCN , isobutane, tetramethylmethane, 2,2,4, trimethylpentane, C_2N_2 , COS , PH_3 , H_2S , CH_3Br , and $\text{C}_2\text{H}_5\text{OH}$. Evidence of hydrogen bond formation is shown for CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CH_3NH_2 , and $(\text{CH}_3)_2\text{NH}$. It is shown that HI and HCN contain a considerable fraction of instantaneously formed double molecules. The gas imperfection of benzene is perfectly normal. The number of instantaneously formed double molecules is estimated for all of the above molecular species.

THE imperfections of many gases may be obtained by using the Clausius-Clapeyron equation together with available experimental heats of vaporization and vapor pressure data. The accuracy in some cases is comparable to that of good direct P.V.T. measurements. In this way we can learn a great deal about the degree of association and the nature of the intermolecular forces in gases for which no direct P.V.T. measurements have ever been made. However, any conclusions based on this indirect method should be verified in other ways before they are regarded as scientific truth.

The Clausius-Clapeyron equation is usually written:

$$dP/dT = \Delta H/T(V - V_l). \quad (1)$$

Here P is the vapor pressure, T is the absolute temperature at which the boiling takes place,

ΔH is the heat of vaporization, and V and V_l are the molal volumes of the vapor and the liquid, respectively. This equation may be arranged into the form:

$$\frac{PV}{RT} = \frac{-\Delta H}{R(1 - V_l/V)(d \ln P/d(1/T))}. \quad (2)$$

In elementary treatments the vapor is usually assumed to be ideal so that $PV/RT = 1$ and the volume of the liquid is neglected in comparison with the volume of the vapor. When these assumptions are made, it is easy to integrate Eq. (2) to express the heat of vaporization directly in terms of the vapor pressure at two different temperatures. The values for the heats of vaporization obtained in this manner with good vapor pressure measurements are usually in error by around six percent. In this paper we

are attributing this deviation to the imperfection of the gas and making it serve a useful purpose. From the experimental measurements of vapor pressure we can calculate $d \ln P/d(1/T)$. If in addition we know ΔH and V_l/V , the right-hand side of the equation is completely determined and we are left with an experimental value of PV/RT .

It is convenient to express the imperfection of the gas in terms of a function, β , defined by the equation:

$$PV/RT = 1 + \beta/V. \quad (3)$$

We have tabulated the observed values of β for a number of substances. Large negative values correspond to association, and we can estimate the percentage of double molecules present.

The equation of state of any gas may be written in the virial form:

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \dots, \quad (4)$$

where $B(T)$, $C(T)$, \dots , are called the second, third, \dots , virial coefficients and are functions of the temperature but not of the pressure. In ordinary P.V.T. measurements one can determine the virials separately by varying the pressure while keeping the temperature constant. This is not possible in our method since we can only consider one pressure for any particular temperature. However, most of the experimental vapor pressure measurements are made at pressures sufficiently low that the contribution of third and higher virials is negligible for a normal gas, and for these we can show that $\beta = B(T)$. For associated gases where β is exceptionally large it is probable that the third and higher virials appreciably affect the value of β .

The argument that $\beta = B(T)$ for normal gases measured at a vapor pressure of around one atmosphere or less depends on the theorem of corresponding states. If we divide the second virial coefficient by the critical volume V_c we get a reduced second virial coefficient $B_r(T/T_c)$, which should be a universal function of the reduced temperature T/T_c . Similarly, we could define reduced third and higher virial coefficients. Hirschfelder, McClure, and Weeks¹ have shown that for a number of normal gases the experimental second virial coefficient agrees reasonably

¹ J. O. Hirschfelder, F. T. McClure, I. S. Weeks, *J. Chem. Phys.* **10**, 201 (1942).

well with that which would apply if energy of interaction of the molecules satisfied a Lennard-Jones potential:

$$E(r) = 4E_m[(r_0/r)^{12} - (r_0/r)^6], \quad (5)$$

where E_m , the maximum energy of interaction between pairs of molecules on collision, is

$$E_m = 0.73T_c k \quad (6)$$

and k is the Boltzmann constant. Now we can make use of the work of Montroll and Mayer² who express the third and fourth virial coefficients for the Lennard-Jones gases in the form:

$$\begin{aligned} C(T) &= -8/3(B(T))^2 \nu_2 \\ D(T) &= 6(B(T))^3 \nu_3. \end{aligned} \quad (7)$$

Here ν_2 and ν_3 are known functions of E_m/kT . The normal boiling point usually corresponds to values of T approximately $0.6T_c$ or

$$E_m/kT = 0.73T_c k / 0.6T_c k = 1.2. \quad (8)$$

For this argument Montroll and Mayer computed that $\nu_2 = 0.019$ and $\nu_3 = 1.13$. For normal gases, in this temperature range, $|B/V|$ is always less than 0.05 so that

$$\begin{aligned} |C/V^2| &< |(8/3)(0.05)^2(0.019)| = 0.0002 \\ \text{and } |D/V^3| &< |(6)(0.05)^3(1.13)| = 0.001. \end{aligned} \quad (9)$$

Therefore, in identifying β with $B(T)$ we are neglecting terms in PV/RT of the order of 0.001 or making an error in $B(T)$ of the order of $22,000 \times 0.001$ of 22 cc per mole. This is about the limit of the accuracy of β which can be attained from experimental considerations.

The ratio of double to single molecules present in the gas at any instant, N_2/N_1 is estimated by the method developed by Hirschfelder, McClure, and Weeks.¹ In place of $B(T)$ we take β and for the van der Waals b for the definitional domain of the double molecules we take $1.75V_c$. Then the equilibrium constant for the formation of double molecules is:

$$K = \frac{N_2 V}{N_1^2} = 1.75V_c - \beta.$$

Since we are usually dealing with a small degree

² According to a private communication from J. Mayer. The development of these higher virial coefficients was subsequently published by E. W. Montroll and J. E. Mayer, *J. Chem. Phys.* **9**, 626 (1941).

TABLE I.

	T°K	- β calc.	- $B(T)$ obs.	
1. H ₂ O	373.16	460	452	
	423.16	287	284	
	473.16	196	197	
	523.16	139	146	
	573.16	97	112	
	623.16	58	89	
2. NH ₃	233.16	516	662 ^a	561 ^b
	239.68	438	593	507
	243.16	443	560	467
	273.16	329	367	319
	293.16	265	290	250
	313.16	217	237	207
3. H ₂	18.2	164 ^c	210	
	20.4	72 ^d	170	
O ₂	90.13	206 ^e	230	
A	87.29	244 ^f	220	
CH ₄	99.54	4090 ^g	340	
	111.55	203 ^g	290	
4. propane	231.04	658 ^h	700	
n-butane	272.66	904 ⁱ	840	
n-heptane	371.51	1300 ^j	1500	
ethene	169.40	428 ^k	430	
propene	225.35	575 ^l	650	
CH ₃ Cl	248.94	527 ^m	680	
CFCl ₃	290.40	831 ⁿ	620	
5. CH ₃ OH	298.16	4190 ^o	2280	
	323.16	2130	1370	
	337.86	1480	1030	
	363.16	905	640	
	383.16	655	440	
Benzene	323.16	1390 ^p	1610	
	353.16	885	1160	
	383.16	746	850	
6. Hg	630.0	2050 ^q	250	

^a Reference 5.^b Reference 9.^c Martinez and Onnes, Comm. Phys. Lab. Univ. Leiden 156b (1922); Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).^d Martinez and Onnes, Comm. Phys. Lab. Univ. Leiden 156b (1922); Eucken, Ber. d. Deut. Phys. Ges. 18, 4 (1916).^e Cath, Comm. Phys. Lab. Univ. Leiden 152d (1918); Giauque and Johnston, J. Am. Chem. Soc. 51, 2300 (1929).^f Born, Ann. d. Physik 69, 473 (1922); Frank and Clusius, Zeits. f. physik. Chemie 42, 395 (1939).^g Henning and Stock, Zeits. f. Physik 4, 226 (1921); Frank and Clusius, Zeits. f. physik. Chemie 42, 395 (1939).^h Kemp and Egan, J. Am. Chem. Soc. 60, 1523 (1938).ⁱ Aston and Messerly, J. Am. Chem. Soc. 62, 1917 (1940).^j Smith, J. Research Nat. Bur. Stand. 24, 229 (1940); Pitzer, J. Am. Chem. Soc. 62, 1224 (1940).^k Egan and Kemp, J. Am. Chem. Soc. 59, 1265 (1937).^l Powell and Giauque, J. Am. Chem. Soc. 61, 2367 (1939).^m Messerly and Aston, J. Am. Chem. Soc. 62, 886 (1940).ⁿ Osborne, Garner, Doescher, and Yost, J. Am. Chem. Soc. 63, 3496 (1941).^o Young, Proc. Roy. Soc. Dublin 12, 374 (1910); Fiock, Ginnings, and Holton, J. Research Nat. Bur. Stand. 6, 881 (1931).^p Dejardin, Ann. de Physique 12, 253 (1919); Fiock, Ginnings, and Holton, J. Research Nat. Bur. Stand. 6, 881 (1931).^q Menzies, Zeits. f. physik. Chemie 130, 90 (1927); W. Kurbatoff, *ibid.* 43, 104 (1903).

of dissociation, to the first approximation:

$$V = \frac{N_1 RT}{P}$$

So that:

$$\frac{N_2}{N_1} = \frac{PV_c}{RT} \left[1.75 - \frac{\beta}{V_c} \right]$$

I. EXPERIMENTAL VERIFICATION OF THE METHOD

Before relying on such an indirect method of determining the imperfections of gases it is obligatory to make a rather extensive comparison between our values of β and those of $B(T)$ calculated from direct P.V.T. measurements. In the cases of NH₃ and H₂O sufficient data are available to permit us to make the comparison over a considerable temperature range. For H₂, O₂, A, CH₄, CH₃Cl, CCl₃F, propane, *n*-butane, *h*-heptane, ethene, and propene we checked our values at a temperature in the neighborhood of the normal boiling point. In Table I, β is compared with the second virial coefficients obtained directly. Most of the values agree within the accuracy of the experimental data considered; only a few values are poor.

1. H₂O

Our values of β for steam were determined from the empirical equation of Keenan and Keyes³ for the vapor pressure as a function of the temperature and from the heats of vaporization of water determined by Osborne, Stimson, and Ginnings.⁴ It was necessary to differentiate the vapor pressure equation to obtain $d \ln p/d(1/T)$. This is probably the largest single source of error in our method. The values of β were compared to those of $B(T)$ calculated from the equation of F. G. Keyes.⁵ The experimental values for steam are exceptionally accurate so that it is not surprising that the agreement between β and $B(T)$ is good.

2. NH₃

Osborne and Van Dusen⁶ determined the heats of vaporization of NH₃ at various temperatures.

³ J. H. Keenan and F. G. Keyes, *Thermodynamical Properties of Steam* (John Wiley, 1936).

⁴ Osborne, Stimson, and Ginnings, J. Research Nat. Bur. Stand. 23, 261 (1939).

⁵ F. G. Keyes, J. Am. Chem. Soc. 60, 1761 (1938).

⁶ N. S. Osborne and M. S. Van Dusen, J. Am. Chem. Soc. 40, 1 (1918).

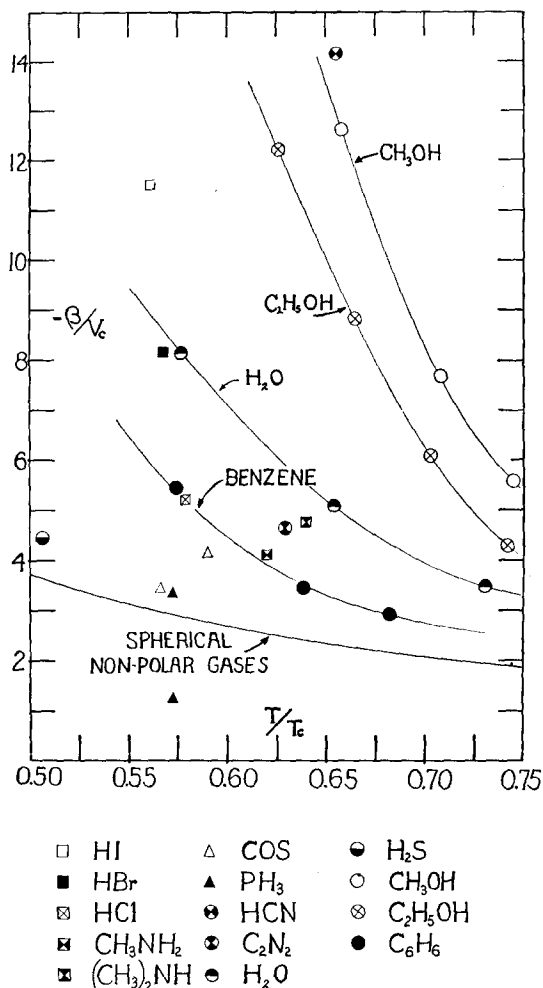


FIG. 1. Reduced second virial coefficients as a function of the reduced temperature.

Overstreet and Giauque⁷ developed an equation for the vapor pressure of NH_3 in terms of the temperature, from 199°K to 242°K. They also determined the heat of vaporization at 239.68°K. This work was done in process of determining the entropy calorimetrically. Cragoe, Meyers, and Taylor⁸ developed an equation for the vapor pressure from -78°C to 70°C. We calculated β from these data.

Keyes⁹ also gives an equation for the virial coefficient of NH_3 . This equation gives us values of $B(T)$ to compare with our values of β . In order to compare our accuracy with that of

various direct P.V.T. determinations, we calculated the second virial coefficient from the previously accepted data for NH_3 as tabulated in a publication of the Bureau of Standards.⁹ The differences between the two relatively accurate P.V.T. determinations of $B(T)$ is of the same order of magnitude as that between β and $B(T)$.

3. Simple Non-Polar Gases

The second virial coefficients for the simple non-polar gases were estimated on the assumption that the molecules obey a Lennard-Jones type of potential. For these calculations we used previously determined values of the molecular constants.¹⁰ These values agree reasonably well with our values of β .

4. Hydrocarbons and Substituted Methanes

These were compared to values extrapolated from experimental data at high temperatures by means of equations developed recently.¹ The value of β for CH_4 at 99.54°K is obviously erroneous and probably due to small experimental errors.

5. Methyl Alcohol and Benzene

Eucken and Meyer¹¹ have measured directly the second virial coefficients for a number of organic substances. They included methyl alcohol and benzene. Their values are compared to ours. The values of $B(T)$ are calculated from their empirical equations. This amounts to a short extrapolation in both cases. At the higher temperatures the agreement is satisfactory, i.e., within 25 percent.

6. Hg

Our value is of doubtful accuracy since the heat of vaporization was determined by W. Kurbatoff in 1903 by a rather crude method. However it is interesting to note that this value is in line with the fact that mercury vapor contains a considerable fraction of double molecules. Actually mercury contains such a large fraction

⁷ R. Overstreet and W. F. Giauque, J. Am. Chem. Soc. **59**, 254 (1937).

⁸ Cragoe, Meyers, and Taylor, Bur. Stand. Sci. Papers **16**, 1 (1920).

⁹ Circular of the Bureau of Standards, No. 142 (1925).

¹⁰ J. O. Hirschfelder and W. E. Roseveare, J. Phys. Chem. **43**, 15 (1939).

¹¹ A. Eucken and L. Meyer, Zeits. f. physik. Chemie **5b**, 452 (1929).

of Hg_2 that its spectrum is well known and spectroscopic constants have been calculated for it. Hildebrand, Wakeham, and Boyd¹² determined the potential energy curve for Hg_2 from this spectroscopic data and Robert Bonner¹³ has estimated from it the second virial coefficient as a function of temperature. The large deviation between β and the calculated $B(T)$ may or may not be significant. Further experimental work on the heat of vaporization and vapor pressure of mercury would be very desirable.

II. APPLICATION OF THE METHOD

Since this method appears to be valid whenever the experimental values of the vapor pressure and heats of vaporization are reasonably accurate, it is interesting to examine data for a number of different molecular species for which there are no direct P.V.T. data. In Fig. 1 we have plotted the values of $-\beta/V_c$ versus T/T_c for a number of substances. V_c and T_c are the critical volume and temperature, respectively. If the equation of corresponding states were valid, all of these points should lie on one curve. Actually the points show no such regularity. The reason for this is that the particular molecules studied here were chosen because of certain unusual properties, i.e., tendency to form hydrogen bonds, asymmetrical shape, large dipole moments, and the like. The reason for the deviations from the corresponding states equation is explained for the individual molecules. In Table II, our results are summarized and references given to all of the experimental data. We have included a column for $\mu^2/T_c V_c$ (where μ is the dipole moment) since the value of this reduced dipole moment should govern the deviation from the corresponding states equation due to dipole effects. The fact that this is not true for molecules forming hydrogen bonds shows that the formation of hydrogen bonds must be considered quite separately from normal dipole behavior. Undoubtedly many of our values of β are unreliable because of errors in the experimental heats of vaporization and vapor pressure, but it is amusing to see what implications could be drawn if we assume that all of our values are correct.

¹² Hildebrand, Wakeham, and Boyd, *J. Chem. Phys.* **7**, 1094 (1939).

¹³ Robert Bonner, unpublished.

Where possible the critical constants were taken from the *International Critical Tables*. In a few cases where no data on the critical volume were available, we estimated the value from the critical temperature and pressure and a value of p_0/RT at the critical conditions equal to that of a similar substance. The dipole moments are those recommended by Smyth.¹⁴

TABLE II.

	$T^\circ\text{K}$	$-\beta$	T/T_c	$-B/V_c$	$\mu^2/T_c V_c$ ($\times 10^{-41}$)	N_2/N_1 (at 1 atmos.)
HI	237.75	1300 ^a	.561	11.50	.30	.077
HBr	206.38	767 ^b	.568	8.14	1.78	.055
HCl	188.07	446 ^c	.579	5.19	3.80	.039
CH_3NH_2	266.84	518 ^d	.620	4.11	2.79	.034
$(\text{CH}_3)_2\text{NH}$	280.04	868 ^e	.640	4.74	1.15	.052
HCN	298.80	1910 ^f	.654	14.16	11.4	.088
Isobutane	261.44	695 ^g				
Tetramethyl- methane	278.59	1090 ^h				
2,2,4, Trimethyl- pentane	372.33	1480 ⁱ				
C_2N_2	251.95	695 ^j	.628	4.65	0	.046
COS	214.03	470 ^k	.566	3.45	.82	.040
	222.87	565 ^l	.590	4.15		.044
PH_3	185.35	379 ^m	.572	3.35	.83	.038
	185.72	143 ⁿ	.573	1.26		.032
H_2S	188.7	410 ^o	.505	4.45	2.63	.037
	212.77	1740 ^p	.570	18.9		.109
CH_3Br	276.66	660 ^q				
CH_3OH	298.16	4190 ^r	.581	35.6	4.67	.180
	323.16	2130	.630	18.1		.088
	337.86	1480	.658	12.6		.061
	363.16	905	.708	7.68		.037
	383.16	655	.747	5.56		.027
$\text{C}_2\text{H}_5\text{OH}$	323.16	2040 ^r	.626	12.2	3.35	.087
	343.16	1470	.665	8.82		.063
	363.16	1020	.703	6.09		.044
	383.16	715	.742	4.28		.032
Benzene	323.16	1390 ^s	.575	5.43	0	.069
	353.16	885	.639	3.45		.046
	383.16	746	.682	2.90		.038

The first reference refers to the source of data on the vapor pressure of the material. The second refers to the source of data on the heat of vaporization. Where only one reference is given, this contains data on both.

^a Henglein and Roth, *Zeits. f. Physik* **18**, 64 (1923); Giauque and Wiebe, *J. Am. Chem. Soc.* **51**, 1441 (1929).

^b Henglein and Roth, *Zeits. f. Physik* **18**, 64 (1923); Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 2193 (1928).

^c Henning and Stock, *Zeits. f. Physik* **4**, 226 (1921); Giauque and Wiebe, *J. Am. Chem. Soc.* **50**, 101 (1928).

^d Aston, Siller, and Messerly, *J. Am. Chem. Soc.* **59**, 1743 (1937).

^e Aston, Eidinoff, Forster, *J. Am. Chem. Soc.* **61**, 1539 (1939).

^f Giauque and Ruehrwein, *J. Am. Chem. Soc.* **61**, 2626 (1939).

^g Aston, Kennedy, and Schumann, *J. Am. Chem. Soc.* **62**, 2059 (1940).

^h Aston and Messerly, *J. Am. Chem. Soc.* **58**, 2355 (1936).

ⁱ Smith, *J. Research Nat. Bur. of Stand.* **24**, 229 (1940); Pitzer, *J. Am. Chem. Soc.* **62**, 1224 (1940).

^j Ruehrwein and Giauque, *J. Am. Chem. Soc.* **61**, 2940 (1939).

^k Kemp and Giauque, *J. Am. Chem. Soc.* **59**, 79 (1937); Frank and Clusius, *Zeits. f. physik. Chemie* **42**, 395 (1939).

^l Kemp and Giauque, *J. Am. Chem. Soc.* **59**, 79 (1937).

^m Stephenson and Giauque, *J. Chem. Phys.* **5**, 149 (1937).

ⁿ Henning and Stock, *Zeits. f. Physik* **4**, 226 (1921); Frank and Clusius, *Zeits. f. physik. Chemie* **42**, 395 (1939).

^o Giauque and Blue, *J. Am. Chem. Soc.* **58**, 831 (1936); Frank and Clusius, *Zeits. f. physik. Chemie* **42**, 395 (1939).

^p Giauque and Blue, *J. Am. Chem. Soc.* **58**, 831 (1936).

^q Egan and Kemp, *J. Am. Chem. Soc.* **60**, 2097 (1938).

^r Young, *Proc. Roy. Soc. Dublin* **12**, 374 (1910); Fiock, Ginnings, and Holton, *J. Research Nat. Bur. Stand.* **6**, 881 (1931).

^s DeJardin, *Ann. d. Physique* **12**, 253 (1919); Fiock, Ginnings, and Holton, *J. Research Nat. Bur. Stand.* **6**, 881 (1931).

¹⁴ C. P. Smyth, *Dielectric Constant* (Chemical Catalog Company, New York, 1931).

1. HI, HBr, HCl

For this series HI has by far the largest value of $-\beta/V_c$ in spite of the fact that its dipole moment is the smallest. Apparently HI is really made up of a considerable fraction of H_2I_2 .

2. CH_3NH_2 and $(CH_3)_2NH$

Dimethylamine has a large value of $-\beta/V_c$ and seems to be largely associated. Methylamine has a somewhat smaller value of $-\beta$ but still contains a considerable fraction of dimers. These results are not surprising since the amines and particularly the diamines have a tendency to form hydrogen bonds. A straight dipole effect should give methyl amine the larger value of $-\beta/V_c$ so that its effect alone should give the opposite order. While the above results are suggestive, they are not conclusive since they might arise from experimental errors.

3. Methyl and Ethyl Alcohol

Both methyl and ethyl alcohols have very large values for $-\beta/V_c$ which would indicate that they contained a considerable fraction of dimers in the gas phase. These results are in keeping with the tendency for the alcohols to form hydrogen bonds. Considerable work has been done on the study of hydrogen bonds formed in liquid alcohol.

4. Benzene

The values of $-\beta/V_c$ for benzene seem perfectly normal and would agree with the corresponding states equation for the second virial coefficients of the hydrocarbons.¹ Benzene molecules are shaped like plates and interfere with each other's rotation in the liquid. (This argu-

ment is used to explain why the benzene made from deuterium has a greater vapor pressure than ordinary benzene.) On this account, we should expect an unusually small number of double molecules. Direct P.V.T. determination of the second virial coefficient of benzene would be particularly useful for theoretical interpretations.

5. HCN

It appears that HCN gas contains an appreciable fraction of instantaneously formed double molecules. This agrees with the conclusion reached by Giauque and Ruehrwein¹⁵ that HCN vapor contains straight chain polymers of indefinite length.

CONCLUSION

1. The Clausius-Clapeyron equation combined with accurate experimental values of the heats of vaporization and vapor pressures suffices to make reasonable estimates of the second virial coefficients for a number of substances for which no direct P.V.T. data is available.

2. The most interesting examples are those molecules which have a tendency to form hydrogen bonds. Our calculations for the fraction of dimers present in HI, dimethylamine, methyl and ethyl alcohol, and HCN should be substantiated or refuted by infra-red spectroscopic observations of the vapors.

3. This method is particularly suitable for use with those compounds whose absolute entropies are determined with great precision by calorimetric methods and accurate heats of vaporization and vapor pressures are determined as by-products.

¹⁵ W. F. Giauque and R. A. Ruehrwein, J. Am. Chem. Soc. **61**, 2626 (1939).