The Theory of OpenTube Distillation Column

Marcel Bertrand and Marcel Rinfret

Letters to the Editor

THIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the first of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge ($8.00 per page) will not be made and no reprints will be furnished free.

The Theory of Open-Tube Distillation Column

MARCEL BERTRAND AND MARCEL RINFRET
Department of Chemistry, University of Montreal, Montreal, Canada
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FOR total reflux and ideal reflux conditions, the H.E.T.P. of an open-tube distillation column was found by Westhaver[1] to be $11vr^2/48D$ where v is the radially averaged velocity, r the radius, and D the molecular diffusion coefficient of the vapor stream.

The graphical representation of the above formula should give a straight line passing through the origin.

The authors[2] have found that the H.E.T.P. varies proportionately with the average velocity of the vapor stream but that the straight line which represents that proportionality does not pass through the origin.

The experiments were conducted in a highly insulated column as suggested by Westhaver.[1]

The results are summarized in Table I and in Fig. 1.

We think that the fact that the curve does not pass through the origin can be explained by a retardation of the equilibrium between the flow of vapor and the reflux film.

The ratio of the number of vapor molecules condensing on a surface, per second, to the total number incident on the surface may be defined as the "condensation coefficient" of the vapor at the surface.

Alty[3] has shown experimentally that the condensation coefficient is not always unity, as one can see in Table II. It can be noted that the molecules which have a zero dipole moment have a condensation coefficient of unity; on the other hand, the coefficient is small for molecules of large dipole moment.

We believe that the attainment of equilibrium is proportional to the number of collisions per second on the liquid surface and also to the efficiency of the collisions. In fact, all the collisions are not efficient according to Alty's results.

By the kinetic theory the number of collisions per second is equal to the number of molecules multiplied by the average velocity of those molecules.

TABLE III.

Constituents	Averaged velocity cm/sec.	Molar fraction	Number of collisions/ cm²/sec.	Collisions of mixture
CHCl₃	24572	0.16	3930	22150
CCl₄	21691	0.84	18220	
C₆H₆	30916	0.36	11130	28690
C₂H₄Cl₂	27441	0.64	17560	
CH₃OH	47791	0.14	6690	39870
C₂H₅OH	38587	0.86	33180	

In Table III are summarized the number of collisions which were calculated for our binary mixtures. We can consider that (1) the retardation is greater when there are less collisions and (2) and still greater when they are less efficient.

Now, if we compare the results shown in Fig. 1 with those in Table III we can come to the conclusion that: (1) The retardation for the $CHCl_3-CCl_4$ mixture is the greatest because the number of collisions is small and, for $CHCl_3$, not very efficient, because the $CHCl_3$ has a large dipole moment and therefore a small condensation coefficient. (2) The retardation for the $CH_3OH-C_2H_5OH$ mixture is almost as large because the efficiency of the very large

TABLE I.

Binary mixtures	Vapor stream velocity cm/sec.	H.E.T.P. cm
CHCl₃ – CCl₄	1.11	61.3
	4.31	95.3
	7.38	122.0
	13.87	193.7
CH₃OH – C₂H₅OH	4.15	42.2
	12.38	54.2
	16.48	61.9
	24.71	72.2
C₆H₆ – C₂H₄Cl₂	11.30	24.1
	16.83	26.6
	22.61	31.4
	28.38	39.4

TABLE II.

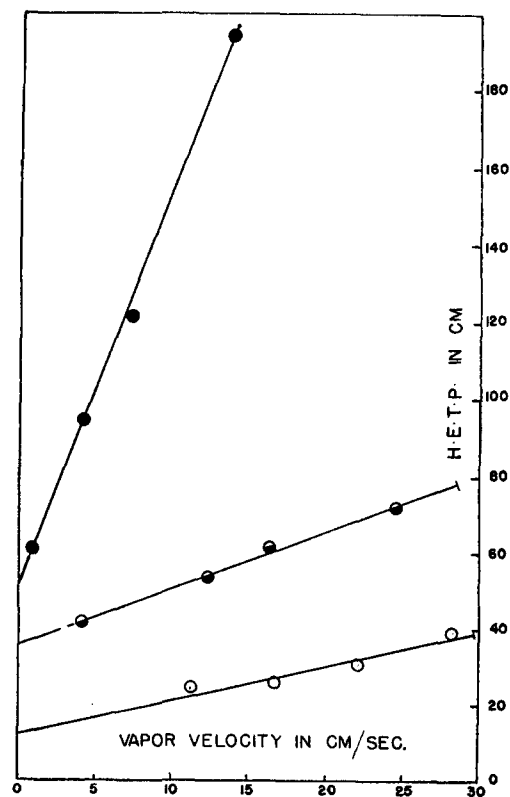| Substances	Condensation coefficient
Benzene	1.0
Carbon tetrachloride	1.0
Benzoic acid	0.29
Water	0.036
Ethyl alcohol	Small

FIG. 1. ● CHCl₃ – CCl₄. ◒ CH₃OH – C₂H₅OH. ○ C₆H₆ – C₂H₄Cl₂.

number of collisions is very small for ethyl alcohol, according to Alty's results, and we can presume the same effect for methyl alcohol which has about the same dipole moment as ethyl alcohol. (3) The retardation of the $C_6H_6-C_2H_4Cl_2$ mixture is small because the number of collisions is large and only the ethylene chloride has a condensation coefficient less than unity.

[1] J. W. Westhaver, Ind. and Eng. Chem. **34**, 126 (1942).
[2] M. Bertrand, Ph.D. thesis, University of Montreal (1950).
[3] T. Alty, Nature **139**, 374 (1937).

Nuclear Magnetic Resonance in Methane*

J. T. Thomas, N. L. Alpert, and H. C. Torrey
Physics Department, Rutgers University, New Brunswick, New Jersey
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NUCLEAR magnetic resonance studies of materials with more than one phase in the solid state have been carried on in this laboratory as a continuation of the earlier work done by one of us.[1]

The most interesting and complete results have so far been obtained in methane. Plots of the thermal relaxation time (T_1) and of the line width (ΔH) vs. absolute temperature are shown in Figs. 1 and 2, respectively.

The technique used has been the pulse method recently described by Torrey.[2] All of the data reported here were taken using a new nuclear resonance cryostat designed and constructed in this laboratory. This cryostat operates on the principle of adiabatic isolation commonly used in specific heat measurements. The cryostat and associated equipment permit the variation, control, and measurement of temperature to within better than 0.1°K in the vicinity of 20°K and lower, and to within better than 0.2°K in the vicinity of 80°K and lower.

The line-width data obtained here on methane do not agree with those previously reported.[1] This is not the case for other materials for which we have obtained close checks. In view of the

FIG. 1.

FIG. 2.

comparatively qualitative nature of the data taken in those early, exploratory experiments on methane, this is not surprising. The absence of any change in line width at the λ-point at 20.4°K eliminates the possibility of a rotational transformation, as originally suggested by Pauling.[3] This conclusion is in agreement with the x-ray observations of Mooy.[4]

The data for T_1 are more complex. The values reported here are reproducible to about one percent above 65°K and to about five percent below 65°K where the line becomes broad. The salient features are: (1) The extremely small value of T_1 in the vicinity of 2 to 4°K. (2) The behavior of T_1 is anomalous in the vicinity of the λ-point and there may be a small discontinuity in T_1 near the λ-point. This will be studied further. (3) There are two dips in T_1 in the solid state, rather than one as might be expected on the basis of the Bloembergen, Purcell, Pound[5] theory. (4) T_1 is continuous across the melting point. (5) The small dip in T_1 just above the melting point is unexpected on the basis of existing theories.

At first we suspected the presence of paramagnetic impurity, particularly oxygen, which might explain (1) above.[6] Since we did not know the impurities in the sample, we condensed a new sample from a tank of Matheson c.p. (better than 99 percent) methane, which is supposed to contain traces of ethane, nitrogen, and carbon dioxide, but no oxygen. This showed roughly the same relaxation times at helium temperatures and gave about the same variation with temperature, according to a few spot checks at various temperatures. We plan to obtain an even purer sample to study this factor as well as other possible impurity effects.

Although data have not yet been taken between 4.2 and 14°K, there is apparently a minimum in T_1 in this range. If we assume that this dip is due to a decrease in the characteristic time[5] τ_c, we obtain values of τ_c which would require the line width to be much narrower than observed in this range. Other explanations are under study. The minimum at 73°K is qualitatively consistent with the line-width data, as predicted by the Bloembergen, Purcell, Pound theory. On the basis of this theory, τ_c is almost constant from about 30°K to about 55°K, after which it starts dropping rapidly almost up to the melting point. There is apparently sufficient activity in the solid at the melting point so that the additional Brownian motion in the liquid phase has little or no effect on τ_c.

A more detailed account of this work as well as our results on other substances will be submitted for publication in the near future.

[1] N. L. Alpert, Phys. Rev. **75**, 398 (1949).
[2] H. C. Torrey, Phys. Rev. **76**, 1059 (1949).
[3] L. Pauling, Phys. Rev. **36**, 430 (1930).
[4] H. H. Mooy, Leiden Comm. **19**, 213d (1931).
[5] Bloembergen, Purcell, and Pound, Phys. Rev. **73**, 679 (1948).
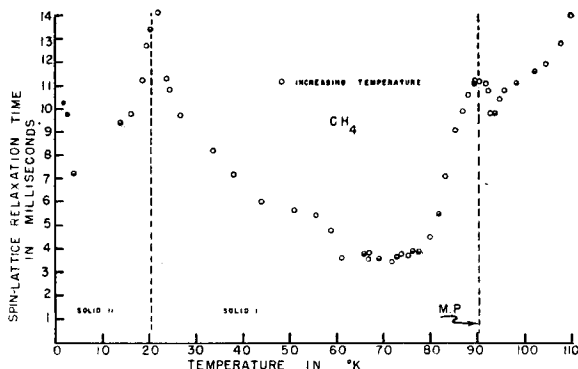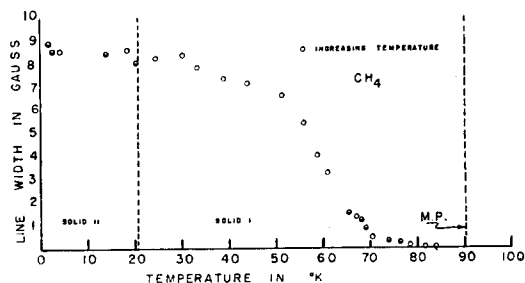[6] N. Bloembergen, Physica **XV**, 386 (1949).

The Infra-Red Spectrum and Molecular Structure of HNCS

L. H. Jones and Richard M. Badger
*Gates and Crellin Laboratories of Chemistry,
California Institute of Technology,*
Pasadena, California
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FROM an examination of the microwave spectra of four isotopic species of isothiocyanic acid, Beard and Dailey[1] recently obtained the following values for the molecular parameters in the ground vibrational state:

$$r_{C-S}=1.57\pm0.01A; \quad r_{N-C}=1.21\pm0.01A;$$
$$r_{N-H}=1.2\pm0.1A; \quad \angle HNC=112°\pm10°.$$

These C−S and N−C distances are not unexpected, but the N−H distance is abnormally long and the HNC angle abnormally