The Separation of Mixtures by Centrifuging

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Citation: J. Chem. Phys. **5**, 993 (1937); doi: 10.1063/1.1749983
View online: https://doi.org/10.1063/1.1749983
View Table of Contents: http://aip.scitation.org/toc/jcp/5/12
Published by the American Institute of Physics

TABLE I. *The Raman spectrum of CH_3CF_3 liquid at −75°.*

Frequency in cm^{-1}	Character	Number of Exciting Lines Scattered from
358 (2)		2
541 (2)	Sharp	3
603 (2)	Sharp	2
829 (5)	Sharp	5
968 (3)		3
1279 (1)		1
1450 (4)	Diffuse	2
2792 (2)		1
2825 (1)		2
2885 (1) ?	Diffuse	1
2974 (5)		8
3040 (4)	Diffuse	5

TABLE II. *The Raman spectrum of $CF_2=CCl_2$ liquid at room temperature.*

Frequency in cm^{-1}	Character	Number of Exciting Lines Scattered from
255 (6)		7
435 (7)	Sharp	4
454 (1)		2
562 (6)		5
622 (4)	Sharp	5
648 (2)	Diffuse	2
883 ($\frac{1}{2}$)	Diffuse	1
1027 (2)	Diffuse	2
1123 (1)		2
1735 (6)		2
1976 ($\frac{1}{2}$)	Diffuse	2

the exposure times varying from one to twenty hours in the case of the liquids. A quinine hydrochloride solution filter between the mercury arc and the tube was used in some exposures on both compounds to determine which of the observed lines were excited by 4358A and which by 4078 or 4047A. This test or an equivalent one is necessary for those cases in which the scattered lines from two or more exciting lines overlap. In Table I the numbers in parentheses adjoining the frequency values indicate estimated relative intensities.

Since CH_3CF_3 gas absorbs fairly strongly in the ultraviolet, the results of experiments on it are not presented separately, and they were of use only in confirming the 3040, 2974 and 829 cm^{-1} lines. The absorption resulted in the photochemical decomposition of the gas. The substance in the liquid form is colorless and showed no absorption in the visible region.

The selection rules[1] for CH_3CF_3, assuming a symmetry of C_{3v}, permit a total of 11 fundamental frequencies in the Raman spectrum, of which 6 would have a polarization $\rho=\frac{3}{4}$. Twelve lines in all were observed, of which the one with a frequency of 2885 cm^{-1} is the only doubtful one. For purposes of comparison it is of interest to set down here the vibrational frequencies obtained for CF_4 in the Raman spectrum[2] and infrared;[3] $\nu_1(1)$, 904; $\nu_2(2)$, 437; $\nu_3(3)$, 1252; $\nu_4(3)$, 635 cm^{-1}. The selection rules for $CF_2=CCl_2$ permit 12 fundamental frequencies to appear in the Raman spectrum (7 with $\rho=\frac{3}{4}$) if the symmetry is assumed to be C_{2v}, while only 11 were observed. Moreover some of the weaker lines may be combinations of overtones.

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October 27, 1937.

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* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 630.

[1] The selection rules for the CH_3CF_3 type molecule were determined by Dr. Fred Stitt.

[2] Yost, Lassettre and Gross, J. Chem. Phys. **4**, 325 (1936).

[3] C. R. Bailey, Hale and Thompson, J. Chem. Phys. **5**, 274 (1937). Eucken and Bertram, Zeits. f. physik. Chemie **B27**, 79 (1934).

The Separation of Mixtures by Centrifuging

The separation of a mixture into its pure constituents by the usual methods such as fractional distillation, fractional crystallization, etc., sometimes is a very slow and tedious process. This is especially true in the case of many constant boiling point mixtures. Therefore, it might be of interest to mention some experiments in which our vacuum type tubular centrifuge was used to separate a mixture of substances of different molecular weights while in the vapor state.

Briefly, the centrifuge consists of a vacuum tight alloy steel tube 2.6 cm (effective) internal diameter and 12.5 cm long, which spins inside a vacuum chamber.[1] The vapor entered the spinning tube at the top through a stainless steel hypodermic needle tube (gauge 15), and the lighter and heavier fractions were collected at the bottom through two coaxial stainless steel hypodermic needle tubes (gauges 15 and 12), communicating with the axis of rotation and the periphery of the spinning tube, respectively. The inlet to the spinning tube was sealed (by vacuum tight oil glands) to a flask containing a mixture (constant boiling point) of carbon tetrachloride and methyl alcohol, and the outlets which collected the lighter and heavier fractions were sealed, also by vacuum tight oil glands, each to a separate trap immersed in dry ice. The system was evacuated and the vapor passed through the centrifuge at the rate of approximately a cubic centimeter of liquid per minute. In each experiment precaution was taken to make sure that practically all of the mixture placed in the flask passed through the centrifuge and was collected in the dry-ice traps; also, that approximately equal light and heavy fractions were collected. Care was taken to insure that each fraction contained only the carbon tetrachloride—methyl alcohol mixture and hence was free of possible impurities such as vacuum pump oil, etc. With the tube or centrifuge spinning 1800 r.p.s. the density of the heavier fraction in the liquid state was roughly 4.7 percent heavier than that of the lighter fraction in the liquid state at the same temperature.

According to the well-known theory for the centrifuging of gases[2] when equilibrium is established

$$K_p/K_p=e^{(M_1-M_2)w^2r^2/2RT}$$

where M_1 and M_2 are the molecular weights of the two gases, respectively, T the absolute temperature, R the gas constant, r the radius of the centrifuge, w the angular velocity in radians per sec., K_p the ratio of the quantities of heavy substance to light substance at the periphery of the rotor, and K_c the ratio of the quantities of the heavy to the light substances at the center of the centrifuge. This equation has been shown to be in agreement with experiment[3] for gases which approximately obey Boyle's law. If it is assumed to hold in the experiment described above, then K_p/K_c comes out 1.7 and the density should have changed by about 5.7 percent, which is within 20 percent of the above experimental value. Therefore, the theory of separation apparently can be depended upon to give at least the right order of magnitude for the separation of a mixture of vapors.

It is interesting to observe that K_p/K_c increases very rapidly with wr or the peripheral velocity of the rotor. With the tubular or other vacuum type centrifuges the only factor which limits the maximum angular velocity, or the wr attainable is the bursting strength of the spinning tube or centrifuge. We have worked with hollow rotors with an effective wr of 5×10^4 cm/sec. and it is probable that with the proper material and construction of rotor that a wr of 6 or 7×10^4 cm/sec. might be obtained. However, assuming only the 5×10^4 cm/sec., $K_p/K_c=446$ for the methyl alcohol-carbon tetrachloride mixture. Consequently the lighter fraction would become almost pure methyl alcohol and the heavier fraction almost pure carbon tetrachloride in a single centrifuging. Obviously by drawing off a smaller amount of the substance to be concentrated, greater purification can be obtained. It is also possible to design a multistage centrifuge which should greatly increase the concentration as well as the speed with which the centrifuging takes place. Therefore centrifuging might become a useful supplement to fractional distillation for the separation of some substances that have different molecular weights.

We are greatly indebted to the Natural Science Division of the Rockefeller Foundation for a grant which has made possible the development of the tubular vacuum type centrifuge.

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University of Virginia,
November 5, 1937.

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[1] For a description and drawings of the centrifuge see Beams, Linke and Skarstrom, Science **86**, 293 (1937), Figs. 1 and 2.

[2] Lindemann and Aston, Phil. Mag. **37**, 530 (1919). Aston, *Isotopes* (Longmans, Green and Co., 1924). Mulliken, J. Am. Chem. Soc. **44**, 1033 (1922); **45**, 1592 (1923).

[3] Beams and Haynes, Phys. Rev. **50**, 149 (1936).

Low and High Raman Frequencies for Water

In a recent note[1] I. R. Rao and P. Koteswaram state that some of the Raman bands for water reported by other workers do not correspond to different frequencies of water excited by the λ2537 mercury line but are ascribable to the $\Delta\tilde{\nu}$3200–3600 band of water excited by lines other than the λ2537 line. The bands at $\Delta\tilde{\nu}$500 and 2150 reported by the writer[2] were ascribed by Rao and Koteswaram to the mercury exciting line λ2464, and $\Delta\tilde{\nu}$175 to λ2345.

The writer assigned the frequencies $\Delta\tilde{\nu}$175, 500 and 2150 to the λ2537 mercury line as the source of excitation for the reason that in the type of mercury lamp employed by him in these experiments, namely "Sc 2537,"[3] there is no line at a wave-length less than λ2537 capable of giving rise to any Raman frequency, hence multiple excitation does not exist. The intensity of the mercury lines λ2345, 2378 and 2464 is less than 1 percent (probably nearer 0.1 percent) of λ2537 in this type of low pressure mercury discharge tube. It is probable that Rao and Koteswaram are not familiar with this lamp. In the ordinary type of mercury burner the lines λ2345, 2378 and 2464 might be sufficiently intense to cause multiple excitation. In the low pressure arc 85 percent of the total energy output of the lamp is confined to the λ2537 line, and because of the low mercury pressure there is no reversal effect. In consequence of this there is an even greater difference between the intensity of the λ2537 line and other mercury lines.

However, to eliminate any possible doubt in the matter, the Raman spectrum of water was redetermined, using an acetic acid and sodium acetate filter between the mercury arc and the Raman tube. This completely absorbed all radiation of a wave-length less than λ2537. There was no change in the Raman spectrum of water, and the bands at $\Delta\tilde{\nu}$175, 500, 1659 and 2150, etc. appeared as previously described.

So far as the frequencies $\Delta\tilde{\nu}$4023 and 5100 are concerned, these have been reported by other workers and have not been observed by the writer. Rao and Koteswaram ascribe these shifts to an excitation by λ2576 and 2652 respectively, yielding therefore $\Delta\tilde{\nu}$3414 and 3383 instead of $\Delta\tilde{\nu}$4023 and 5100. However, no multiple excitation by the mercury lines λ2576 and 2562 has been observed during the study of many organic compounds. If these were the source of multiple excitation, duplicate lines would have appeared in these studies. It is probable, therefore, that difference in types of lamps may make inapplicable the conclusions of Rao and Koteswaram insofar as they apply to the low mercury pressure source of illumination.

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Carnegie Institution of Washington,
November 8, 1937.

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[1] J. Chem. Phys. **5**, 667 (1937).

[2] J. Chem. Phys. **5**, 166 (1937).

[3] Hanovia Chemical Mfg. Co., Newark, N. J.

Corrections to: A Method for Deriving Expressions for the First Partial Derivatives of Thermodynamic Functions.

(J. Chem. Phys. **5**, 792 (1937))

The symbols C_P and C_V in the equations for basic vireds at the bottom of the first column, page 793, have been interchanged. The corrected equations are:

$$dT_P=1=T/C_PdS_P,$$
$$dT_V=(\partial V/\partial P)_T=T/C_VdS_V,$$
$$dV_P=(\partial V/\partial T)_P=dS_T.$$

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