

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

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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 experiment³ 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 ωr 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 ωr attainable is the bursting strength of the spinning tube or centrifuge. We have worked with hollow rotors with an effective ωr of 5×10^4 cm/sec. and it is probable that with the proper material and construction of rotor that a ωr 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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Rouss Physical Laboratory,
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November 5, 1937.

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 note¹ 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 $\lambda 2537$ mercury line but are ascribable to the $\Delta\tilde{\nu} 3200$ –3600 band of water excited by lines other than the $\lambda 2537$ line. The bands at $\Delta\tilde{\nu} 500$ and 2150 reported by the writer² were ascribed by Rao and Koteswaram to the mercury exciting line $\lambda 2464$, and $\Delta\tilde{\nu} 175$ to $\lambda 2345$.

The writer assigned the frequencies $\Delta\tilde{\nu} 175$, 500 and 2150 to the $\lambda 2537$ 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 $\lambda 2537$ capable of giving rise to any Raman frequency, hence multiple excitation does not exist. The intensity of the mercury lines $\lambda 2345$, 2378 and 2464 is less than 1 percent (probably nearer 0.1 percent) of $\lambda 2537$ 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 $\lambda 2345$, 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 $\lambda 2537$ 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 $\lambda 2537$ 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 $\lambda 2537$. 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 $\lambda 2576$ 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 $\lambda 2576$ 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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November 8, 1937.

¹ *J. Chem. Phys.* **5**, 667 (1937).

² *J. Chem. Phys.* **5**, 166 (1937).

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

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

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

$$\begin{aligned}dT_P &= 1 = T/C_P dS_P, \\dT_V &= (\partial V/\partial P)_T = T/C_V dS_V, \\dV_P &= (\partial V/\partial T)_P = dS_T.\end{aligned}$$

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