

The results appear in Table II. The corrections used in making the calculations have been described in the previous papers.

It will be seen that the maximum deviation from the mean value is 0.26%.

The heat of solution of sodium chloride under the same conditions, as determined with the former calorimeter,<sup>1b</sup> was 787.5 cal. per mole. The difference between this and the above results may easily be accounted for by the uncertainty in the values used for the specific heats of the sterling silver and the platinum from which the calorimeters were constructed.

The results obtained show that a fair degree of accuracy may be attained with a calorimeter of this type while requiring the use of only small quantities of material.

Grateful acknowledgment is made to the National Research Council of Canada for a grant to aid in this research and also for a Studentship held by one of us, during the tenure of which the work was carried out.

### Summary

A small calorimeter is described with which heats of solution may be determined using 4 cc. of solvent and corresponding amounts of solute. The heat capacity of the calorimeter is approximately 1 cal.

Several determinations of the heat of solution of sodium chloride at the same concentration gave results which never differed from a mean value by more than 0.26%.

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[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE CHEMICAL LABORATORY OF THE U. G. I. CONTRACTING COMPANY]

## THE NEAR INFRA-RED ABSORPTION BANDS OF SOME HYDROCARBONS

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This report, which is a continuation of earlier papers,<sup>1</sup> is on the measurements of the wave lengths of the near infra-red absorption bands of liquid pentane, decane and tetradecane. It also contains some observations on the structure of the 8744 Å. band of benzene and the 8767 Å. band of toluene.

The apparatus used, namely, source of continuous radiation, cells, gratings and densitometer, as well as the methods of photography and of measurement of wave lengths, were the same as those described in the papers referred to above. In addition, a Hilger prism spectrometer of

<sup>1</sup> Barnes and Fulweiler, THIS JOURNAL, 49, 2034 (1927); *J. Opt. Soc. Am.*, 15, 331 (1927).

the constant deviation type D with camera attachment was employed. Due to its low dispersion, results of importance were observed which did not appear on the plates obtained with the gratings. We also used to advantage a filter<sup>2</sup> of solarized green celluloid which Dr. Pettit of Mt. Wilson Observatory kindly sent to us.

On account of the diffuseness of the absorption bands of the paraffins compared with those of the benzene derivatives, the measurements of their wave lengths are not quite so accurate but are believed to be within 20 Å. or 0.002 $\mu$ . We have, therefore, recorded the following results using  $\mu$  instead of Å. as the unit. They are the means of many measurements made upon the center of the bands from a number of photographic plates, never less than two, of each substance in cells 30 and 80 cm. long.

Each of the two strongest absorption bands of the paraffins in the region investigated is a doublet whose component wave lengths will be designated by  $\lambda_1$  and  $\lambda_2$ , and their frequencies by  $\nu_1$  and  $\nu_2$ , the difference of which,  $\Delta\nu$ , is given in the fifth column of figures in Tables I and II, where the measurements were made on plates taken with the plane grating and the six-foot concave grating.

### Results

Table I gives the results for the absorption band at 0.92 $\mu$ , approximately.

TABLE I  
WAVE LENGTHS AND FREQUENCIES OF THE 0.92 $\mu$  BAND OF PARAFFINS

	$\lambda_1(\mu)$	$\lambda_2(\mu)$	$\nu \times 10^{-12}$	$\nu \times 10^{-12}$	$\Delta\nu \times 10^{-12}$
Pentane	0.912	0.932	329	322	7
Decane	.913	.936	328	321	7
Tetradecane	.914	.934	328	321	7

Table II gives the results for the absorption band at 0.75 $\mu$ , approximately.

TABLE II  
WAVE LENGTH AND FREQUENCIES OF THE 0.75 $\mu$  BAND OF PARAFFINS

	$\lambda_1(\mu)$	$\lambda_2(\mu)$	$\nu \times 10^{-12}$	$\nu \times 10^{-12}$	$\Delta\nu \times 10^{-12}$
Pentane	0.745	0.760	403	395	8
Decane	.747	.763	401	393	8
Tetradecane	.747	.763	401	393	8

These tables show that the frequencies of the bands of the hydrocarbons of the paraffin series are lower than the frequencies of the corresponding bands of the benzene series, and that the frequencies tend to decrease as the mass of the molecule becomes larger, which is also the case with the benzene series. They also show that the frequency difference,  $\Delta\nu$ ,

<sup>2</sup> Pettit, *Astrophys. J.*, **66**, 46 (1927).

which is of interest for the calculation<sup>3</sup> of the moments of inertia of the molecules, depends on the order of the band in the series, if one assumes that these bands are due to an unharmonic rotational and vibrational oscillator in the molecule. In this connection, the results obtained by Meyer, Bronk and Levin<sup>4</sup> for gaseous butane, hexane and octane are worthy of comparison with the above.

As is usually the case with the so-called vibrational-rotational bands in gases, the shorter wave length component in both the above bands in all three liquid paraffins has the stronger intensity, the densitometer graphs giving their relative intensity as very nearly 4 to 3.

Using the prism spectrometer with cells 80 cm. in length, the paraffins showed, in addition to the above strong, double bands, two weak single bands with wave lengths approximately  $0.81\mu$  and  $0.97\mu$ . The accurate measurement of these bands will require much longer absorption cells than those used up to the present time. However, it is important to note that under similar conditions the benzene derivatives do not show a corresponding series.

The slopes of the curves on the densitometer graphs of the strong absorption bands  $8744 \text{ \AA}$ . of benzene and  $8767 \text{ \AA}$ . of toluene suggested that they also were doublets, the details of which were lost due to the large dispersion of the gratings. Plates were therefore taken with the prism spectrometer of the absorption of these two liquids in cells of 80 cm. length and they showed clearly the results as predicted. The differences in their frequencies,  $\Delta\nu$ , were the same within the limit of measurement and had a value of  $3 \times 10^{12} \text{ sec.}^{-1}$ . With the same length of cell the benzene band at  $7133 \text{ \AA}$ . and the toluene band at  $7142 \text{ \AA}$ . showed no sign of doubling.

### Summary

The near infra-red absorption bands of liquid pentane, decane and tetradecane, which were photographed with grating and prism spectrometers, were each found to consist of a doublet and a singlet series. The frequencies of the doublet series of the paraffins were lower than the frequencies of the corresponding series of the benzenes. The frequency difference for the paraffin doublet band at  $0.92\mu$  was  $7 \times 10^{12} \text{ sec.}^{-1}$ , while for the band at  $0.75\mu$  it was  $8 \times 10^{12} \text{ sec.}^{-1}$ .

The  $0.874\mu$  band of benzene and the  $0.877\mu$  band of toluene are also close doublets with a frequency difference of  $3 \times 10^{12} \text{ sec.}^{-1}$ .

<sup>3</sup> Kemble, "Molecular Spectra in Gases," *Bulletin National Research Council*, 1926, p. 11 *et seq.*

<sup>4</sup> Meyer, Bronk and Levin, *J. Opt. Soc. Am.*, **15**, 257 (1927). •