

### Summary

1. The specific heats of two crystalline forms of cyclohexanol were measured down to about 13.5°K.
2. The "mean" temperature and heat of transition between the two crystalline modifications were obtained.
3. The heat of fusion of cyclohexanol was measured.
4. The entropy calculations show that both crystalline forms have the same entropy at 0°K. within the limits of experimental error.
5. The entropy and free energy of liquid cyclohexane at 298.1°K. have been calculated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEW HAMPSHIRE]

## THE PREPARATION OF PHOSPHENYL CHLORIDE

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Since derivatives of phosphenyl chloride have been desired from time to time during rare metal research, it was decided to investigate certain methods involved in the preparation of this substance with the hope of finding some suitable and convenient procedure.

The cheapest method appeared to be that of passing vapors of benzene and phosphorus trichloride repeatedly through a red-hot tube. The equipment required was very similar to that employed in the earlier method for the preparation of diphenyl. After giving this method a thorough trial it was discarded owing to the fact that such a long time was required to produce a small quantity of the product. It appeared to the workers that without doubt a considerable amount of the phosphenyl chloride was decomposed owing to the long heating as it passed through a considerable length of the red-hot quartz tube. It therefore seemed desirable to use an apparatus similar to that described in the preparation of diphenyl,<sup>1</sup> in which a glowing ribbon of nichrome was suspended in an atmosphere of benzene vapors. In this case the difficulty was to find a suitable ribbon or filament which would withstand the action of the vapors. The only material which resisted attack and fusion was a large carbon filament which was very carefully removed from a large and antiquated electric light bulb. Unfortunately in this case the filament kept gradually increasing in diameter due to the deposition of carbon, thereby requiring a gradual increase in current throughout the run. It was noticed, however, that much better yields were obtained than by the previous method.

<sup>1</sup> Lowe and James, *THIS JOURNAL*, **45**, 2666 (1923).

The writers found that equipment which was transparent and which allowed the product to be quickly removed from the hot surface gave the best yields since the process could be more easily controlled by observation. The next change made in the diphenyl equipment was the substitution of the ribbon by a heating unit which was unattacked by the vapors in the reaction chamber. The heater which was tried out consisted of a winding of nichrome protected by a quartz tube. This type of heating unit required a different kind of reaction chamber, of a form not unlike that of a common condenser jacket. A study of the accompanying figure will give a better idea of the apparatus. The mixture of benzene

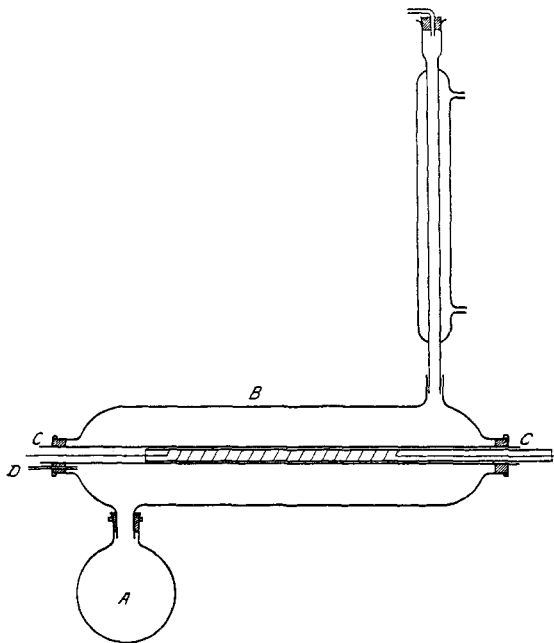


Fig. 1.

and phosphorus trichloride was placed in flask A which is connected to the reaction chamber B by means of a rubber stopper. The upper outlet of the reaction chamber was connected to a reflux condenser. This connection should either be sealed or else a ground joint, since rubber tubing must be changed after every run. The heating element is placed in the interior central portion of the quartz Tube CC which is made tight by alundum cement over a few turns of asbestos rope. Carbon dioxide was admitted to the reaction chamber through the small Tube D. The reaction chamber, dimensions 60 cm.  $\times$  15 cm., was made of Pyrex glass.

In commencing the operation, the liquid in A was heated until all the air in the reaction chamber had been displaced by vapor. At this point

the heating current was turned on and the temperature of the quartz tube raised to a good red heat, care being taken to keep the temperature below carbonization. Under the right conditions the phosphenyl chloride could be observed flowing back to the flask along the bottom of the reaction chamber, the temperature of the latter being too high to allow much of the benzene and phosphorus trichloride vapors to condense. While no attempt was made to determine the maximum yield for an eight-hour run, it appeared that under the best conditions at least one kilo should be obtained *without any carbonization* with an equipment of this capacity.

This reaction chamber may be applied to other reactions where the vapor is heated to some definite temperature and where the reacting substances have similar boiling points. An interesting test was made in the case of the production of acetamide from acetic acid. The latter was just saturated with dry ammonia gas at the boiling point. This crude ammonium acetate was placed in the flask A and boiled while the temperature of the quartz tube was raised to  $245^{\circ}$  on the inside. As soon as the odor of acetic acid appeared at the top of the air condenser attached to the upper outlet of the reaction chamber, ammonia gas was slowly admitted through the small Tube D. When the speed of the ammonia gas was correctly adjusted practically nothing but steam was given off at the top of the condenser. The temperature of the escaping vapors was maintained at about  $101^{\circ}$ . At the end of a three hours' run it was found that the contents of the flask solidified to a mass of crystals on cooling. Fractional distillation showed that the product consisted almost entirely of acetamide. Under these conditions practically the theoretical amount of acetic acid was converted into acetamide.

In conclusion, it may be said that plans are being made to try out certain other reactions, involving this heating and cooling effect, and also the use of catalysts under such conditions.

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