

Summary

1. The inner ammonium salt of 2-amino-4-glyoxalinesulfonic acid has been prepared. On boiling with sodium hydroxide, the sodium salt of the acid is obtained.
2. 2-Hydroxy-4-glyoxalinesulfonic acid has been prepared.
3. 2-Phenyl-4-glyoxalinesulfonic acid has been prepared.

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NORMAL VALEROLACTONE. II. ITS VAPOR PRESSURE

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During the course of a study of the chemical and physical properties of *n*-valerolactone under way in this Laboratory, it became desirable to verify the statement that this compound distils without decomposition¹ at 206–207°. A determination of its vapor pressure, which hitherto has not been reported, seemed to afford the most direct method of approach in the attack on this problem.

Experimental Procedure

The *n*-valerolactone used in this study was prepared by the reduction of levulinic acid as described by one of us.² That which was used for experimentation was dried over anhydrous sodium sulfate and redistilled, the fraction boiling at $125.3 \pm 0.2^\circ$ (68 mm.) serving for the vapor pressure measurements.

Vapor pressure measurements were made over the temperature range 69 to 203.4° by the dynamic method of Ramsay and Young³ and the static method described by Smith and Menzies.⁴ In both methods pressures were read directly from a manometer with the aid of lenses. They are accurate to ± 0.2 mm. The necessity of making stem corrections was avoided in the dynamic method³ by suspending the thermometer in the vapor pressure flask. All observed thermometer readings in the static method⁴ were corrected for stem exposure. Two series of measurements were made by each method.

It was found that the vapor pressure curve as plotted in the usual manner from the data obtained by the dynamic method³ of measurement can be expressed by the empirical equation $\log P = -2540.44/T + 8.2059$. Similarly, the corresponding expression for the data obtained by the static

¹ Messerschmidt, *Ann.*, **208**, 97 (1881).

² Schuette and Sah, *THIS JOURNAL*, **48**, 3163 (1926).

³ Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

⁴ Smith and Menzies, *THIS JOURNAL*, **32**, 1412 (1910).

method⁴ of measurement is $\log P = -2558.42/T + 8.2544$. Furthermore, it was observed that if a composite curve be drawn of the 59 pairs of readings obtained by the two methods of vapor pressure measurement, and an equation fitted to it, there is presented a picture of the relative sensitiveness of these procedures to any decomposition of the lactone that might take place. The deviation plot (Fig. 1) illustrates this situation by showing the differences under the above condition between the observed and calculated pressures at any given temperature. For reasons which will become apparent later, the data obtained by the static method together with the pertinent equation are deemed to be less accurate than the former.

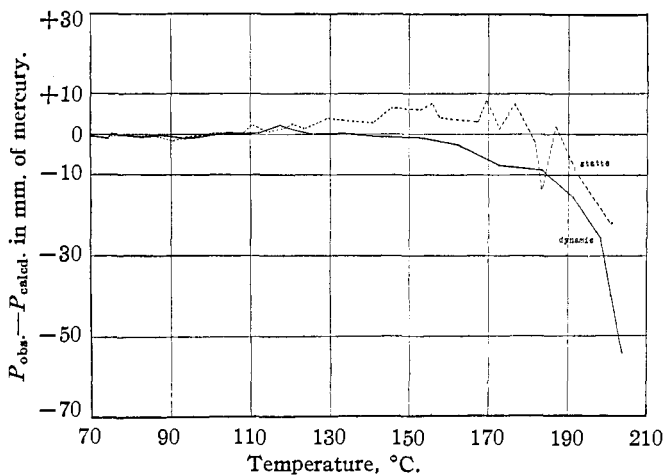


Fig. 1.—Deviation between observed and calculated pressures by two methods of measurement.

Discussion

At the completion of the determination by the Ramsay and Young method, a slight carbonaceous residue was noted in the apparatus where an occasional drop of the lactone had fallen from the thermometer bulb to the hot surface of the flask. The observed pressures for this method agree very well with the calculated up to about 160°, but beyond this temperature there is considerable disagreement, which increases with rising temperature (Fig. 1). Since both of the above facts point to decomposition, it was decided to check these data by using a different method⁴ for determining the vapor pressure. Since in this, the isoteniscopic or static, method the material under examination is constantly exposed to view, decomposition becomes visual, if not real, by a change in color of the liquid in question. In this particular instance the lactone showed the first signs of discoloration at about 170°, the color gradually increas-

ing until at the completion of the run it was a dark brown. The observed and calculated values for the vapor pressure again were found to agree very well at low temperatures and to vary considerably at higher temperatures (Fig. 1).

These data bring out the following points: (1) at low temperatures the values for the two methods agree very well; (2) as the temperature increases the pressures recorded by the static method are higher than those by the dynamic; and, (3) in both cases, the observed values are less than the calculated at the higher temperatures.

Conclusion

In the light of the information obtained in this study it appears that *n*-valerolactone does undergo some decomposition as it approaches its boiling point at atmospheric pressure. This statement is further verified by the darkening of the compound. The isoteniscopic method of determining vapor pressure is in this instance more sensitive to this decomposition. This is due to the fact that the resulting decomposition products are confined to the small space between the liquid in the bulb and in the U-tube rather than being swept out of the apparatus as is the case in the Ramsay and Young apparatus, hence affecting the observed pressure much more. That the values obtained by this latter method actually were lower bears out this conclusion. At first thought it might be expected that if decomposition takes place the observed values would be higher than those calculated. However, this is not necessarily the case since the values $\log P/(l/T)$ give a straight line only when the heat of vaporization is a constant with change of temperature. There is no necessity for deeming the heat of vaporization of valerolactone to be a constant; in fact it is very probable that the calculated values would be still lower were it not for the compensating effect of decomposition.

The method most sensitive to decomposition, *i. e.*, the isoteniscopic,⁴ does give a better agreement with the calculated pressures at higher temperatures, which justifies the above reasoning.

Summary

1. The vapor pressure of *n*-valerolactone has been determined and may be expressed by the equation $\log P = (-2540.44/T) + 8.2059$, which holds for temperatures up to 160°.

2. It was found that decomposition takes place as *n*-valerolactone approaches its boiling point at atmospheric pressure.

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