

Substituting this in the Clapeyron–Clausius equation gives $L = RA$ and

$$\Delta H_1 = R(A_w - A_s) \quad (3)$$

ΔH_1 values obtained from this equation appear as circles in Fig. 3 for the sake of comparison with calorimetric data. Table V contains the ΔH_1 values calculated from calorimetric data, column 4, and from vapor pressure data, column 3, for the solutions on which vapor pressure measurements were made (see Table I).

TABLE V

PARTIAL MOLAL HEATS OF SOLUTION OF WATER IN MANGANOUS NITRATE SOLUTIONS, IN JOULES

Soln.	Concn., <i>m</i>	ΔH_1 from v. p.	ΔH_1 from heat data
1	1.14	+ 480	- 55
2	2.53	+ 993	- 274
3	3.51	- 107	- 436
4	4.34	+ 173	- 730
5	5.96	- 849	-1314
6	7.38	-1453	-1930
7	8.36	-2356	-2399
8	9.74	-2230	-3115
9	10.94	-5604	-3766

The discordance in ΔH_1 is explained by the large change in slope of the $\ln p$ vs. $1/T$ line resulting from a small error in vapor pressure measurement. Assuming that the 40° measurement is most accurate, an error of 0.1 mm. at 25° for the most dilute solution changes the calculated ΔH_1 by about 1000 j. For this reason the ΔH_1 values from calorimetric data are much more reliable.

Vapor pressure data at 25° , tabulated in parentheses in Table I, were calculated by means of Eqs. 2 and 3, making use of ΔH_1 from calorimetric

data and the measured vapor pressures at 40° . Thus the slopes of the $\ln p$ vs. $1/T$ lines (plotted as broken lines in Fig. 1) for these solutions were fixed. Freezing points obtained from the intersection of these broken lines with the saturated solution curves fall nicely on the freezing point–composition curves obtained experimentally.⁴

The relative error in calorimetric measurements is about the same as in previous work.^{5,6} The absolute error may be slightly greater because of the inability to apply heat corrections to infinite dilution. On the basis of work done with other systems, this correction is estimated to be of the order of 1 kj. In the thermodynamic calculations, however, the difference between two experimentally determined values are involved in each case; hence, since final concentrations do not vary greatly (0.02 to 0.12 *M*) this very nearly constant error cancels out to a large extent.

Summary

Vapor pressure data for the system manganous nitrate–water are given for concentrations up to 24 *m*. They include vapor pressures for the unsaturated, saturated, and supersaturated solutions and for mixtures of the crystals of two hydrates.

The heat of solution of manganous nitrate anhydride has been measured, and the heats of dilution of solutions of the salt have been measured for concentrations up to 24 *m*.

Certain thermodynamic properties have been calculated for these two sets of data and comparison of the results made.

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Optically Active Vasopressor Amines

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Two amines have been resolved for the purpose of comparing the pharmacological action of their optical antipodes. These compounds are β -phenyl-*n*-propylamine² and *N*-methyl- β -phenyl-*n*-propylamine.³

Experimental⁴

Resolution of β -Phenyl-*n*-propylamine.—Seventy-two grams of β -phenyl-*n*-propylamine, supplied by the Wm. S.

Merrell Co., and 36 g. of *l*-malic acid (mole ratio, 2:1) reacted in 200 ml. of absolute alcohol and the mixture was allowed to stand in ice for several hours. Fifty-one grams of the salt crystallized and was filtered. This was divided in halves and one-half was recrystallized four times from 90–95% alcohol. It had then reached its maximum rotation. The recrystallization liquors were used in recrystallizing the second half. The quantity of pure dextro β -phenyl-*n*-propylamine neutral *l*-malate obtained was 27.5 g., a yield of 51%; m. p. $182-4^\circ$; $[\alpha]^{25}_D$ 21.9° (*c*, 4; water).

Twenty-four grams of the levo amine recovered from the resolution mother liquors was treated in absolute alcohol with 12 g. of *d*-malic acid prepared by the procedure of

(1) Wm. S. Merrell Fellow.

(2) Hartung and Munch, *THIS JOURNAL*, **53**, 1875 (1931).

(3) Woodruff, Lambooy and Burt, *ibid.*, **62**, 923 (1940).

(4) The melting and boiling points reported are not corrected.

Dakin.⁵ Four recrystallizations from alcohol gave 13.5 g. of pure levo β -phenyl-*n*-propylamine neutral *d*-malate and 4 g. more was obtained from the mother liquors; m. p. 182–184°; $[\alpha]^{25D} -21.9^\circ$ (*c*, 4; water).

The resolution of the β -phenyl-*n*-propylamine by the tartrate salt was very slow. The salt, prepared by mixing the *dl*-amine with *d*-tartaric acid in mole proportions of 1:1, was recrystallized from alcohol twenty-three times, the last three recrystallizations changing the specific rotation from 31.2° to 31.7° (*c*, 4; water). The yield of the recovered amine was 10–15%; b. p. 102° (20 mm.); $[\alpha]^{25D} 35.4^\circ$ (*c*, 2; absolute alcohol).

Anal. Calcd. for C₉H₁₃N: neut. eq., 135.1. Found: neut. eq. with methyl red, 138.3.

The salt prepared by treating the *dl*-amine with *d*-camphoric acid in mole proportions of 1:1 was recrystallized eighteen times from a mixture of equal parts of alcohol and ethyl acetate, the last three recrystallizations changing the specific rotation from –12.6 to –12.9° (*c*, 3.2; water). This salt contained the levo form of the amine.

Resolution with camphorsulfonic acid and menthoxyacetic acid was also extremely slow in ethyl acetate.

Resolution of N-Methyl- β -phenyl-*n*-propylamine.—This compound was much more difficult to resolve than the previous, unmethylated one. The malate did not crystallize. N-Alkylation lowers the melting points of the salts of an amine and often makes resolution more difficult.

Seventy-six grams of N-methyl- β -phenyl-*n*-propylamine, supplied by the Wm. S. Merrell Co., and 118 g. of *d*-camphorsulfonic acid were dissolved in 1200 ml. of ethyl acetate. After cooling in ice for several hours, 65 g. of salt was filtered off. This was recrystallized by dissolving in about 0.8 its weight of absolute alcohol, carefully adding 5–6 volumes of ether, and allowing to stand in ice for a short time. After 6 recrystallizations, 11 g. of pure dextro N-methyl- β -phenyl-*n*-propylamine *d*-camphorsulfonate

(5) Dakin, *J. Biol. Chem.*, **59**, 7 (1924).

was obtained; m. p. 118–19°; $[\alpha]^{25D} 28.8^\circ$ (*c*, 4; water). By working up the recrystallization liquors, 8.3 g. more was obtained; total yield, 19.3 g. or 20%.

The amine was recovered from 18.3 g. of the salt by liberating it with sodium hydroxide, extracting with ether, drying and distilling. The yield was 7 g., a 92% recovery; b. p. 103° (21 mm.); $[\alpha]^{25D} 32.2^\circ$ (*c*, 2; absolute alcohol).

Anal. Calcd. for C₁₀H₁₅N: neut. eq., 149.14. Found: neut. eq., 150.0.

The levo form was obtained with *d*-mandelic acid. Thirty-eight grams of N-methyl- β -phenyl-*n*-propylamine recovered from the mother liquors of the above resolution reacted with 38 g. of *d*-mandelic acid in 30 ml. of absolute alcohol. The salt was precipitated with 200 ml. of ether. In subsequent recrystallizations, the salt was dissolved in about 0.5 its weight of absolute alcohol and ether equal to 9–10 times the volume of alcohol used was added. The clear, supersaturated solution was allowed to stand in ice for a short time while crystallization took place. After 12 recrystallizations, 8.5 g. of pure levo N-methyl- β -phenyl-*n*-propylamine *d*-mandelate was obtained; m. p. 86–7°; $[\alpha]^{25D} 39.8^\circ$ (*c*, 7; water). From the mother liquors 4.5 g. more was obtained; total, 13 g.

The levo amine was recovered from 15.4 g. of the salt in the manner employed for the dextro form. The yield was 7 g., a 92% recovery; b. p. 101–102° (19 mm.); $[\alpha]^{25D} -31.7^\circ$ (*c*, 2; absolute alcohol).

Summary

1. β -Phenyl-*n*-propylamine has been completely resolved with *l*- and *d*-malic acids.
2. Both antipodes of N-methyl- β -phenyl-*n*-propylamine have been obtained by resolution with *d*-camphorsulfonic acid and *d*-mandelic acid.

COLUMBUS, OHIO

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The Reaction of the Grignard Reagent with Esters of Highly Hindered Acids

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Failure to obtain tertiary carbinols from benzoylmesitylene and Grignard reagents¹ does not necessarily preclude the possibility of preparing them from mesitoic esters and the Grignard reagent. Morton and Peakes² found, in fact, that 2,4,6-tribromotriphenylcarbinol was formed by the action of phenylmagnesium bromide on methyl 2,4,6-tribromobenzoate but could not be made by the action of this reagent on 2,4,6-tribromobenzophenone. Whereas the carbonyl

group of esters is less reactive than that of ketones, it seemed that in highly hindered molecules this difference might be outweighed by the small size of the OR group as compared to that of the phenyl radical.

As a test of this possibility certain alkyl and aryl esters of mesitoic acid have been prepared and treated with the Grignard reagent. Evidence of reaction was obtained in all cases. Alkyl mesitoates when treated with alkylmagnesium halides yield mesitoic acid and the alkyl halide formed from the alkyl group of the ester and the halogen

(1) Fuson, Armstrong and Speck, *J. Org. Chem.*, **7**, in press (1942).
 (2) Morton and Peakes, *THIS JOURNAL*, **58**, 2110 (1933).