

acids occurs at the outer region and increases as it approaches the heartwood. When the heartwood is reached, a material increase in resin acid is noted, but whether the inner or outer heartwood has the larger or smaller percentage of resin acids is dependent upon their respective extractive contents.

**FREE FATTY ACIDS.** This constituent increases in per cent as it passes from the newly formed sapwood to the inner sapwood where it reaches a maximum; then the percentage of fatty acids decreases as it approaches the pith.

**VOLATILES.** This fraction usually increases in per cent as it approaches the pith of the tree.

**ESTERS.** In heartwood the percentage of esters decreases from the outer heartwood to the pith. In some instances the percentage continues to increase as it approaches the outer sapwood; in others it tends to decrease.

**UNSAAPONIFIABLES.** In general, the percentage of unsaponifiable is the least at the outer sapwood and increases, in some cases, to a maximum in the outer heartwood and then decreases as it approaches the center of the tree.

It is interesting to note that the composition of the outer middle heartwood in stand III indicates that it is apparently in the transition stage from sapwood to heartwood. The relatively low resin acid content, together with the slight increase in unsaponifiable material in this outer heartwood region, suggests that this transitional deposition of extractives was taking place.

#### APPLICATION OF RESULTS

In seeking means for effectively utilizing the potential chemical products from ponderosa pine, it was found that this wood contained a sufficient quantity of extractives to warrant the possible removal and recovery of these materials from the lumber and from forest and mill wood waste. Preliminary investigations have shown that it is possible to extract all or a large portion of the extractives from lumber; the result is a further improvement in the lumber offered by manufacturers; in addition, a commercial volume of extractive products may become available from this wood. The amount of recoverable extractables is not uniformly distributed throughout the trunk of the tree. The average extractive content in sapwood is usually within the limits 2.0 to 9.8% of the weight of the dry wood, while the heartwood extractables are usually within the limits 3.5 to 31.5% of the weight of the dry wood. The greater quantities of extractives

are obtained from the lumber and wood waste originating from the butt portion of the trunk and from that portion of the tree containing massed pitch areas.

The acetone extractives, whether from the heartwood or sapwood, contain, in addition to resin acids and terpenes, free fatty acids, fats, and unsaponifiable material. Thus the extractives differ from gum oleoresin formed by wounding the tree by the presence of these aliphatic and unsaponifiable substances. The percentage of each of these entities is not uniformly distributed throughout the tree but depends from which part of the log the extractives are obtained. In the case of heartwood extractives, the products found in approximate order of quantity present are: resin acids, free fatty acids, unsaponifiable, esters, volatile, water soluble, and water and ether insoluble. In sapwood extractives these entities are found in the following order: free fatty acids, resin acids, water soluble, esters, unsaponifiable, water and ether insoluble, and volatile. Since the commercial value of these extractives is contingent in part upon the quantity and exact nature of its entities, the identification of each of these products is under investigation by this laboratory.

#### ACKNOWLEDGMENT

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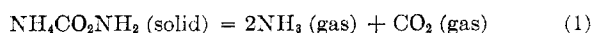
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# Dissociation Pressure of Ammonium Carbamate

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**T**EMPERATURE-pressure relations for the dissociation of solid ammonium carbamate into gaseous ammonia and carbon dioxide have been measured by several investigators. (1-5). The reported values are divergent; at a total pressure of 40 atmospheres the divergence is as much as 17 atmospheres. Briggs and Migrdichian (1) measured the dissociation pressure of ammonium carbamate over temperature range 10° to 45° C. and obtained very consistent data. They also studied the effect of excess ammonia or carbon dioxide and found excellent agreement with the mass law according to the equation:



The present paper covers a study of the dissociation pressure of solid ammonium carbamate over the temperature range 35° to 83° C. and in the absence of an excess of either gaseous reactant. From the vapor pressure data the free energy of dissociation and the heat of dissociation have been derived.

#### PREPARATION OF SOLID AMMONIUM CARBAMATE

Solid ammonium carbamate was prepared directly in a 50-cc. sample bulb (Figure 1) which later was connected to the pressure-measuring system. Stoichiometric proportioning of the reactants, as was employed by Briggs and Migrdichian (1), proved to be unnecessary. The carbamate was deposited in the bulb from

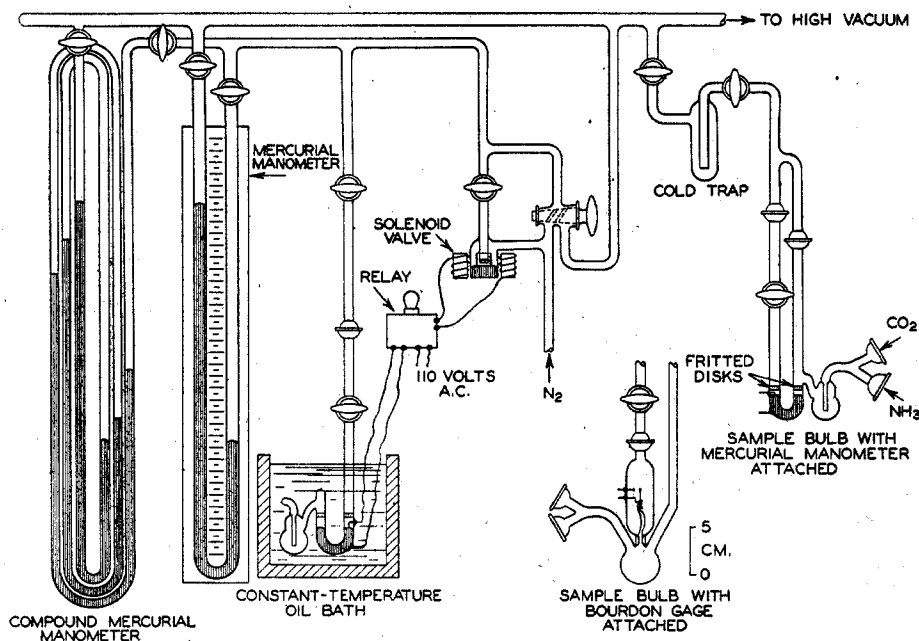


Figure 1. Apparatus for Preparing Ammonium Carbamate and Measuring Its Dissociation Pressure

a roughly equimolar mixture of ammonia and carbon dioxide which was charged at a rate of 1 liter per minute. Deposition of carbamate in the inlet and outlet tubes was prevented by maintaining the temperature of the tubes at 100° C. The gases, which were of commercial grade, were dried thoroughly to prevent the formation of ammonium carbonate and bicarbonate. The carbon dioxide first was washed with acid permanganate and then was dried successively with sulfuric acid and Dehydrite. The ammonia was dried with freshly pulverized fused potassium hydroxide. In preliminary trials in which the sample bulb was cooled with dry ice, expansion of the product on warming to room temperature shattered the bulb. This indicated either a high coefficient of expansion or a phase change in solid ammonium carbamate between -78° C. and room temperature. In subsequent work, therefore, the bulb was cooled in an ice-salt bath.

The ammonium carbamate was purified by alternate partial vaporization and evacuation through a vacuum line that contained a trap cooled with dry ice. The sample was first warmed until the dissociation pressure reached 700 to 800 mm. of mercury, then was cooled with a mixture of dry ice and acetone, and the

The pressure of dissociation of solid ammonium carbamate into gaseous ammonia and carbon dioxide was measured over the temperature range 35° to 83° C. The results, when plotted as  $\log P$  against  $1/T$ , fall on the same straight line as the data of Briggs and Migrdichian for the range 10° to 45° C. The combined data of the two studies are represented by the equation:

$$\log P \text{ (mm. Hg)} = -2741.9/T + 11.1448 \text{ (283° to 355° K.)}$$

The slope of the curve defined by this equation indicates that the heat of dissociation of ammonium carbamate, if assumed to be constant over the experimental range of temperature, is 37.6 kg.-cal. per mole. This value agrees with calorimetrically determined values reported previously. The equation is applied also in the derivation of the free energy of dissociation.

system was evacuated to  $10^{-4}$  mm. of mercury. After three such cycles of degasification, the sample was assumed to be free of foreign gases. On completion of the purification step, all the tubes joining the sample bulb were sealed off, except a short control manometer. The purified sample was not weighed but was estimated to be 0.2 to 0.4 gram.

Each preparation was checked for quality by comparison of its dissociation pressure at an arbitrarily selected temperature of 34.5° C. with the value interpolated from the data of Briggs and Migrdichian (1). About one third of the preparations were discarded because their dissociation pressures exceeded the adopted tolerance of 1 mm. of mercury deviation from the interpolated value of 170 mm. of mercury. None of the preparations yielded a pressure of less than 170 mm. at 34.5° C.

#### MEASUREMENT OF DISSOCIATION PRESSURE

In the technique used for the pressure measurements, the autogenous dissociation pressure was allowed to come to equilibrium at a given temperature with the gases exposed only to the sample bulb and the short control manometer. The control manometer was a null-point instrument with sealed-in electrical contacts in a circuit that automatically balanced the dissociation pressure with nitrogen pressure. The measuring manometer was in the nitrogen system, as Figure 1 shows.

The control manometer used for pressures above 1000 mm. was a glass Bourdon gage that established electrical contact at the tip of the free end of the elastic element. This gage had the advantage that it presented only glass surface to the products of dissociation, but its sensitivity to temperature introduced a significant correction factor at pressures below 1000 mm. At these lower pressures, therefore, a mercurial control manometer was used. A correction factor representing the pressure required to establish electrical contact was determined for each type of gage and was added algebraically to the observed dissociation pressures.

The balancing pressure was obtained from a nitrogen cylinder through a reducing valve. The dissociation pressure was balanced by continuously bleeding a small amount of nitrogen from the system to a vacuum and intermittently introducing nitrogen under pressure through a solenoid valve that would pass a slow stream of gas under a differential pressure of about 10 cm. The valve consisted of an 8-mm. tube that terminated with a fritted glass disk slightly above a pool of mercury in an integral jacket to which the nitrogen source was connected. A cylindrical iron plunger surrounded the 8-mm. tube and floated on the mercury. A solenoid surrounding the jacket pulled down the plunger and thereby raised the mercury surface sufficiently to seal the fritted disk and prevent the passage of nitrogen. The solenoid was actuated through a vacuum tube relay and the contacts in the null-point manometer. At equilibrium the intermittent action of the solenoid caused fluctuations of less than 0.2 mm. in the level of mercury in the measuring manometer.

Pressures up to 1000 mm. were measured on a mercurial manometer with a 12-mm. bore. One leg of the manometer was evacuated to  $<10^{-4}$  mm., which made the manometer absolute within the accuracy of the readings. To eliminate parallax, a glass mirror scale and a sliding hairline index were employed for

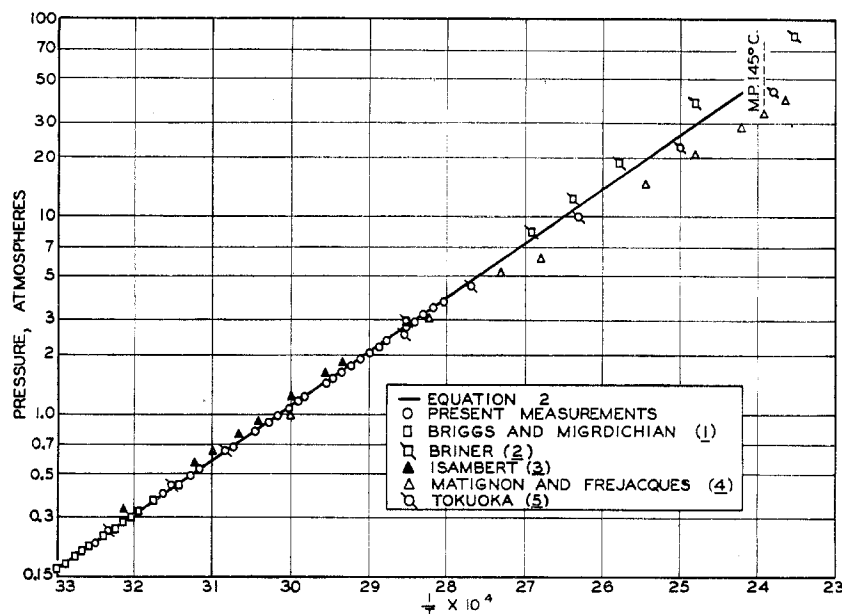


Figure 2. Dissociation Pressure of Solid Ammonium Carbamate

reading the manometer. The pressure readings were corrected to 0° C. for the expansion of glass and mercury.

Pressures above 1000 mm. were read on a three-stage compound mercurial manometer in which the interstage spaces were filled with freshly boiled distilled water. As with the simple manometer, the final leg of the compound manometer was evacuated. The manometer was mounted on a heavy paper scale that differed from the glass scale by less than 1 part in 1000. The pressure differentials in the three stages of the manometer, corrected for the head of water in each stage, were added to give the total pressure. The total pressure was corrected to 0° C. for the expansion of mercury.

The sample was heated in a thermoregulated oil bath. The temperature of the bath was estimated to the nearest 0.01° C. with a calibrated thermometer; the over-all accuracy probably was  $\pm 0.1^\circ$  C. The attainment of equilibrium was ensured by

approaching equilibrium from both the high- and the low-pressure sides. The pressure was read at half-hour intervals until three successive readings agreed within 0.5 mm.

#### DISCUSSION OF RESULTS

Table I gives the measured dissociation pressures. Of the data previously reported, only those of Briggs and Migrdichian (1) fall on the same straight line with the present measurements when plotted as the logarithm of the pressure in millimeters of mercury against the reciprocal of the absolute temperature. Application of the method of least squares to the combined data of Briggs and Migrdichian and of the present work yields the following equation for the dissociation pressure of solid ammonium carbamate:

$$\log P = -2741.9/T + 11.1448 \quad (283^\circ \text{ to } 355^\circ \text{ K.}) \quad (2)$$

where  $P$  = pressure, mm. of Hg  
 $T$  = absolute temperature

The average deviation of the present measurements from Equation 2 is  $\pm 0.4\%$  and the maximum deviation is 1.4%; the corresponding values for the data of Briggs and Migrdichian are  $\pm 0.3$  and 1.3%, which are of the same magnitude as for an equation representing Briggs and Migrdichian's data alone. Figure 2 compares calculated and measured dissociation pressures.

If it is assumed that solid ammonium carbamate dissociates according to Equation 1 and that the vapor is a perfect gas system,

$$p_{\text{NH}_3} = \left(\frac{2}{3}P\right)^2, \quad p_{\text{CO}_2} = \frac{1}{3}P$$

$$K_p = \frac{4}{27}P^3$$

Values of the dissociation constant,  $K_p$ , as calculated from smoothed dissociation pressures derived from Equation 2, are presented in Table II together with values for the free energy of dissociation as calculated from the relation:

$$\Delta F^\circ = -RT \ln K_p$$

The heat of dissociation corresponding to Equation 1, as calculated from the slope of the vapor pressure line in Figure 2 on the assumption of constancy of the heat of dissociation, is 37.6 kg.-cal. per mole of solid ammonium carbamate. This value agrees with calorimetrically determined values (3) but is lower than the heat of dissociation calculated by Krase (3) from the dissociation pressure data of Briner (2).

In this paper no correction of measured pressure to fugacity has been made. A trial calculation, assuming the absence of mixture effect, indicates that, at the melting point, the fugacity of the mixed gases would be about 10% lower than the pressure, which is within the error introduced by extrapolation.

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TABLE I. DISSOCIATION PRESSURE OF AMMONIUM CARBAMATE

Temp., °C.	P, Mm. Hg	Temp., °C.	P, Mm. Hg	Temp., °C.	P, Mm. Hg
34.49	170.1	56.98	688.7	68.91	1327
34.55	171.2	58.26	743.7	70.43	1459
34.59	170.9	59.31	790.1	71.74	1551
42.99	294.2	59.83	812.5	73.18	1673
43.18	295.1	61.24	881.9	74.40	1805
46.48	366.8	62.09	924.2	76.47	1998
47.53	388.9	62.09	925.7	77.30	2093
50.92	479.2	62.13	927.2	78.82	2264
52.19	517.2	65.20	1096	80.27	2456
54.73	603.2	66.19	1158	81.81	2659
55.00	610.2	67.20	1223	83.33	2856
55.78	641.6	67.56	1248	83.38	2864

TABLE II. FREE ENERGY OF DISSOCIATION OF SOLID AMMONIUM CARBAMATE

Temp., °C.	P, Atm.	$K_p$ , Atm. <sup>3</sup>	$\Delta F^\circ$ , Cal./Mole
0 <sup>b</sup>	0.0167	$6.90 \times 10^{-7}$	7700
20	0.0811	$7.90 \times 10^{-5}$	5500
40	0.3212	$4.91 \times 10^{-3}$	3310
60	1.078	$1.86 \times 10^{-1}$	1110
80	3.153	4.64	-1080
100 <sup>b</sup>	8.223	$8.23 \times 10$	-3270
120 <sup>b</sup>	19.45	$10.90 \times 10^2$	-5460
140 <sup>b</sup>	42.33	$11.23 \times 10^3$	-7660

<sup>a</sup>  $K_p = \frac{4}{27}P^3$ , where  $P$  is dissociation pressure in atmospheres.

<sup>b</sup> Extrapolated.