THE HEAT CAPACITIES OF ACETALDEHYDE AND PARALDEHYDE, AND THE HEAT OF TRANSFORMATION OF ACETALDEHYDE INTO PAR-ALDEHYDE.—BY D. LeB. COOPER, B. Sc., Department of Chemistry, Dalhousie University, Halifax, N. S.

In 1865 Kekule and Zincke (A. 162, 125-1865) noticed the fact that acetaldehyde under the influence of a number of catalysts polymerized into two products, the nature of the polymerization depending upon the temperature at which the reaction took place. Above O° C. acetaldehyde changed into paraldehyde, and below that temperature to metaldehyde, both of the polymers having the same empirical formula but different structural formulae. Fehling (Ann. 27, 319) noticed that during the conversion to paraldehyde there was a large heat change. The work of Turbaba (Zeit. Phy. Chem. 38, 505.—1901) established the fact that the point of equilibrium is independent of the catalyst used, and gave at the same time measurements of the rate of reaction under the influence of various catalysts, deduced from measurements of volume change, and density measurements. By volume change he found the equilibrium at 50.5°C to be 33.36-35.23 per cent acetaldehyde, by density measurements 33.87 per cent acetaldehyde and 66.13 per cent paraldehyde. The speed of the reaction varied greatly with the catalyst used, but in the case of acids was roughly proportional to the concentration of the hydrogen ion. Roozeboom(Prec. K. Akad. Wetensch, Amsterdam.) found at 41.7°C. (the Natural Boiling Point of the equilibrium mixture) the equilibrium to be 53.7 mols per cent. paraldehyde, and at 6.8°C. (Natural Freezing Point) 88.1 mols per cent. Holleman (Zeit. Phy. Chem. 43, 129.—1903) gives the following numbers for the natural points and the equilibrium at those points;

88.3 mols percent paraldehyde at 6.75°C.
53.4 mols percent " 41.6° C.

According to Hess' Law the heat of change should be positive and equal to the difference between the heats of combus-

tion of the two substances. Berthelot and Delepine (Compt. rend. 130.—1900) found the heat of combustion of acetaldehyde to be 297,150 cals. per mol. Louginine's figure for paraldehyde is 813,200 cals. per mol. From Hess' Law the heat of change should therefore be

$$838500 - 813200 = 25300 \text{ cals.}$$

The method for the determination of the heat of change described elsewhere required the specific heat of paraldehyde and acetaldehyde over the range 16°-18°C. The work was extended to include the range -78.5°C. to 100°C. for paraldehyde, and -182.5°C. to 17°C. for acetaldehyde. The latent heats of fusion were determined directly from the heat capacity curves.

Apparatus and Manipulation.

The ordinary form of a Richard's Adiabatic calorimeter was used, adapted to the needs of the experiment by having inserted in a removable top to the outer container a tube of diam. 2 cm., and sufficiently long to extend well above the surface of the water in the outer vessel of the calorimeter. A Beckmann thermometer compared as well as possible against a mercury thermometer standardized by the Reichanstalt was inserted in the outer bath. The difference in temperature between the calorimeter proper and the outer bath could be read to .0003°C., and kept constant to .0006°C. after the large primary heat change was completed.

Neglecting small errors the error of the method depended almost entirely on the accuracy with which the change in temperature of the inner calorimeter and its contents could be read. An average change in temperature was .500°C., deviation .005°C. The approximate heat capacity of the substance and container for this change in temperature was 2000 cals., for the glass container alone 400 cals. The approximate maximum error in the final result would therefore be one per cent.

After unsuccessful attempts to use brass, and ordinary glass vessels, as containers for the liquids, the materials were sealed in thin walled Pyrex glass vessels which had been thoroughly cleaned by treatment in the usual manner with

steam, and thoroughly dried. At the end of the determinations
the melting point of the paraldehyde remained unchanged.
The acetaldehyde showed some traces of resins which may
have been caused by slight traces of impurities in the glass.

The Container was allowed to remain in the constant
temperature bath kept at the desired temperature for one
hour, and in the calorimeter for 8 minutes after any detectable
heat change had ceased. The transfer from the constant
temperature bath to the calorimeter could be accomplished
very quickly, so no appreciable error was introduced. The
adequacy of the time of cooling and the time the container was
allowed to remain in the calorimeter was proven by two mea-
surements; 1. a measurement of the time of cooling of paralde-
hyde to -78.5, and 2. a measurement of the time elapsing,
between the entry of the cooled container and its contents in a
constant temperature bath,   By measurement number two
it was also shown that packing the container with copper gauze
offered no advantage.

Purification of Materials.

Paraldehyde—Commercial paraldehyde was distilled,
and the fraction between 123°-124° collected for the prepara-
tion of the pure paraldehyde. The melting point of this frac-
tion varied between 10° and 11°C. in different runs. The
material thus obtained was refluxed over sodium for two
hours and again distilled from over the sodium and collected
in well cleaned Pyrex flasks.   The effect of the sodium is to re-
move any traces of water in the paraldehyde, and to resinify
any acetaldehyde remaining from the former distillation.
The melting point of this material was 12.30°C.   By fractional
crystallizing this material the melting point after four such
crystalizations rose to 12.50°C. and there remained constant.
It was assumed that paraldehyde with this melting point was
pure. Following are some of the melting points ascribed to
pure paraldehyde;

Holleman	12.55°
Turbaba	12.61°-12.58°
Lieben	12.00°

The pure paraldehyde was kept in Pyrex flasks closed with a well waxed cork stopper. At the end of three months the melt-point remained unchanged.

Acetaldehyde.

The fraction of paraldehyde distilling between 123°-124°C. was placed in a distilling flask fastened to a spiral condenser. The condenser had at the other end a reverse adapter cooled by a freezing mixture of ice and salt. A few drops of 50% sulphuric acid was added to the paraldehyde and on gentle heating the mixture boiled (41.8°C) and acetaldehyde distilled over. Direct distillation of the mixture according to Holleman (ibid) gives a mixture containing 1.5 mols per cent of paralde-hyde, which condenses in the reverse adapted used. The freezing point of the liquid thus obtained was not tested, and since some doubts concerning the purity of the liquid arouse later it is the intention of the author to try another method of purification, and repeat the measurements with a new lot of acetaldehyde. The freezing point of acetaldehyde is given by Holleman as -118.0°C. and by M. Chavanne as -123.45°C.

Experimental Results.

Paraldehyde and Acetaldehyde.—Table 1 represents the experimental data on paraldehyde, table 2 that on acetalde-hyde. Column 1 gives the temperature of the constant temperature bath, and column two the mean heat capacity per gram from that temperature to 17.0°C. The heat capacity per gram of Pyrex glass corrected to 17.0°C. is given in table No. 3.

TABLE NO 1. Paraldehyde.		TABLE NO. 2. Acetaldehyde.	
1.	2.	1	2
−78.5°	51.35	−182.5°	109.45
−46.0°	43.18	−131.0°	90.0
− 0.0°	30.70	−127.4°	87.9
− 0.0°	7.575	−106.5°	58.0
50.0°	13.89	− 98.5°	53.3
100.0°	33.41	−78.5°	43.90
S = super cooled liquid		−47.0°	32.7

TABLE NO. 3.

1.	2.
–182.5°	23.86
–127.4°	21.30
–98.5°	18.07
–78.5°	15.69
–50.0°	11.30
–46.0°	10.83
100.0°	15.13
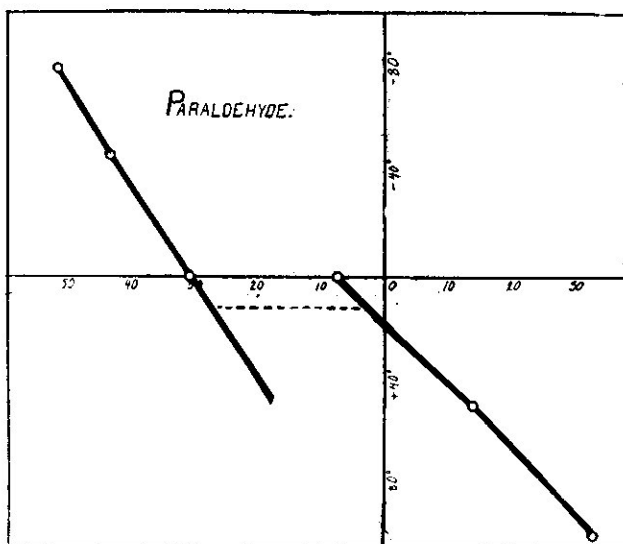
The heat capacities of the paraldehyde and acetaldehyde were plotted and the curves shown obtained. From the curves the latent heats of fusion are; for paraldehyde 25.2 cals, for acetaldehyde 17.6 cals per gram at M.P. -118°C. Louginine and Dupont (Bl. Soc. Chim. 4, 9, 223.) give 25.02 for the latent of fusion of paraldehyde.

Acetaldehyde.

Pyrex Glass.
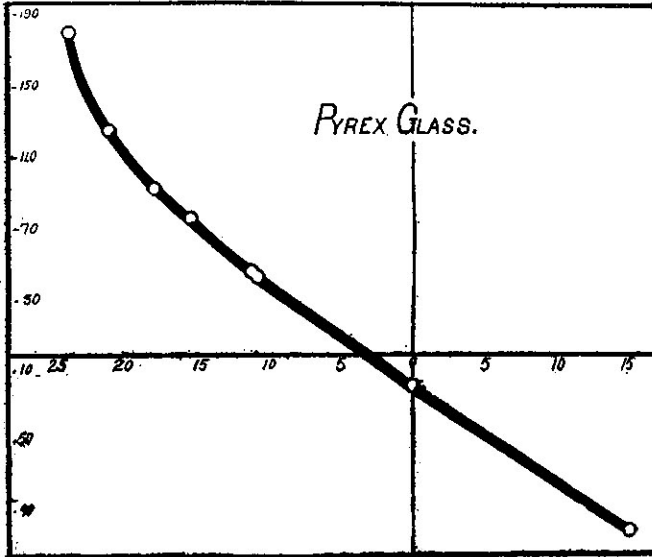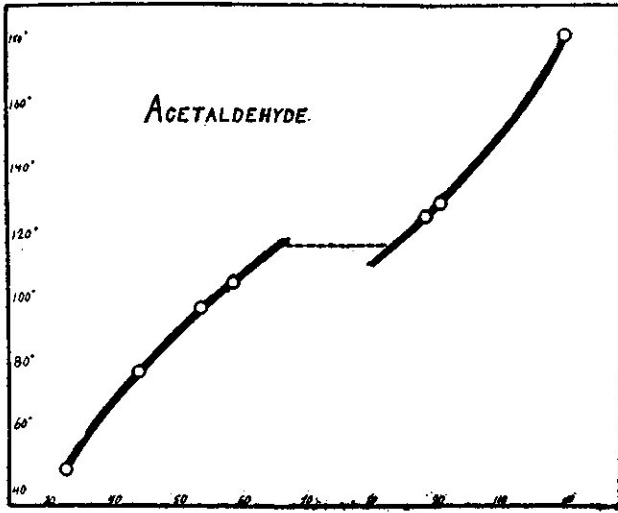
The Determination of The Heat of Change.

Evperimental Method.—Paraldehyde of B. P. 123°
was distilled as described elsewhere, and the acetaldehyde thus
obtained, containing 1.5 mols per cent of paraldehyde was
placed in a glass vessel closed at one end and drawn out to a
narrow tube at the other.   A small inner tube containing sul-
phuric acid 50% and so constructed that when in the vessel
containing the acetaldehyde the surface of the tube extended
well above the surface of the aldehyde, was dropped through
the opening in the container.   The acid was thus prevented
from reaching the aldehyde till it was desired that the reaction
should proceed.   The tube was sealed in such a manner that a
thread could be attached to both ends.   It was allowed to re-
main suspended in the calorimeter in an upright position till
its contents had assumed the same temperature as the contents
of the calorimeter and a reading of the Beckmann thermometer
taken.   The container was then inverted without removing
it from the water of the calorimeter by drawing on the thread
attatched to its bottom, thus allowing the acid in the small
enclosed tube to reach the acetaldehyde.   The reaction pro-
ceeded almost immediately.   Readings were taken at suitable
intervals till three successive readings were the same within
the error of reading the thermometer.   After the apparent
finish of the reaction the container was righted and inverted
several times to make certain that all the material had reacted.

Experimental results.—A mean of two determinations
of the heat of change gives 20495 cals. which is less by 4850 cals.
than the value calculated from the heats of combustion.

The calculation was made as follows; the value shown by
the calorimeter was calculated, and allowance made for the
1.5 mols. percent of paraldehyde contained in the original
samp'e of acetaldehyde.   By interpolation on the curve of
densities with the change in composition and the curve for the
change in equilibrium with the change in temperature it was
found possible to obtain a value for the equilibrium mixture at
any temperature at which the measurements were made.   Cor-
rections were then made for the equilibrium mixture.

The determination of the relation of the composition of mixtures of paraldehyde and acetaldehyde to the density was made in a density bulb standardized with mercury.   The measurements of the composition of the solution were made by volume only in small pipettes.   Following are the results obtained.   Column 1 mols per cent paraldehyde, column 2 the observed density; at 19.3°C.

1	2
0.0	.7834 (from tables).
1.5	.7958
17.0	.8676
29.0	.8999
45.0	.9312
100.0	.9976
Equilibrium Mixture	.9978

The density curve, and the curve for the equilibrium mixture compiled from the work of Holleman, Turbaba, and the above, are given below.
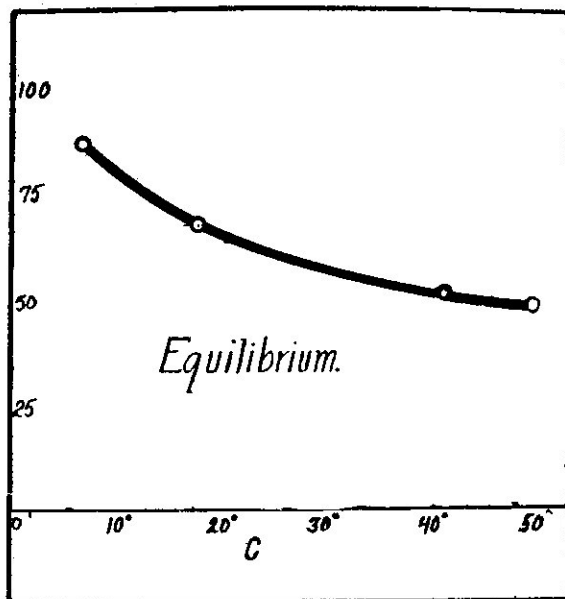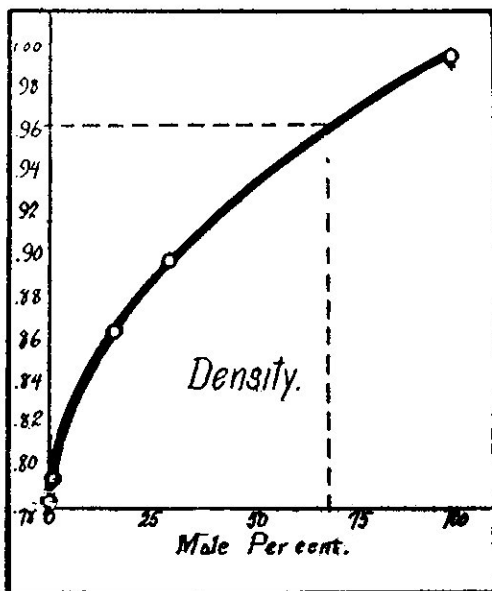
Summary.

1.   The heat capacities of paraldehyde, and acetaldehyde for various temperatures are given.   2.   The latent heat of fusion for both substances has been determined from the heat capacity curve.   3.   The heat of transformation of acetaldehyde into paraldehyde is given.   4.   A heat capacity curve for Pyrex glass from -182.5° to 100°C. is shown.