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CARBONATE AND ISO-PROPYL BENZOATE

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The vapor pressures of propylene carbonate and iso-propyl benzoate were measured by the comparative ebulliometric method. The range of vapor pressures were from 24.8 mm Hg to 620 mm Hg for propylene carbonate and from 56.2 mm Hg to 760 mm Hg for iso-propyl benzoate. To correlate the experimental data the Antoine and the Clausius-Clapyron equations were used and hence the constants of these equations were derived. The method of least squares was used for curve fitting.

It was concluded that the vapor pressure data obtained in this work does not completely satisfy the Clausius-Clapyron equation, which is indicative that the heat of vaporization of both compounds depend on, and vary with, the boiling temperature. On the other hand, the data showed excellent agreement with the Antoine equation. The maximum deviation calculated for the Antoine equation was on the order of 0.06 percent for propylene carbonate and 0.03 percent for iso-propyl benzoate.

Vapor Pressure Determination of Propylene
Carbonate and Iso-Propyl Benzoate

by

Manouchehr Gojgini

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VAPOR PRESSURE DETERMINATIONS OF PROPYLENE CARBONATE AND ISO-PROPYL BENZOATE

INTRODUCTION

The experimental apparatus designed in this project was similar to the one designed by Swietoslowski (19). The vapor pressure of propylene carbonate (1-2-propanediol cyclic carbonate) and iso-propyl benzoate were measured by the comparative ebulliometric method. Double-distilled water was used as a reference.

Any liquid compound which has a boiling point of less than 300° C can be studied with this apparatus, however, the poor heat transmitting fluid (silicon fluid) used for the experiment limited this capability to 232° C.

The ebulliometer was used to measure the boiling and condensation temperature of the compounds. Under the experimental condition any decomposition and polymerization as well as any contamination by corrosion or leakage could be detected.

In order to determine the relationship between the vapor pressure and the temperature, the data were fitted to the Clausius-Clapyron and the Antoine equations. The method of least squares was used for curve fitting. The calculated values were compared with the experimental data and the percentage deviation was determined. There are no previously published vapor pressure data

available for these two compounds. There was no possibility for comparison.

Due to the high purity requirement for vapor pressure determination an extended period of time was spent in purifying propylene carbonate, which practical grade was obtained from Matheson Coleman and Bell Co.

THEORETICAL BACKGROUND

The vapor pressure temperature relationship, which was first introduced by Clapyron has been used to find the vapor pressure correlation equations. Equations (1) through (6) are taken from the book by Nesmeynon (10).

$$dp/dT = \Delta H / (T \Delta V) \quad (1)$$

Nernst introduced the integrated form of the Clapyron equation:

$$\log P = \Delta H_0 / (2.3RT) + (3.5/R) \log T - (aT/4.6R) + \text{Const.} \quad (2)$$

or

$$\log P = A - B/T + CT + D \log T \quad (3)$$

usually in practice it is permissible to ignore the last term, and use the below form:

$$\log P = A - B/T + CT \quad (4)$$

The constants A, B, and C must be determined experimentally.

The Nernst equation reduces to the Clausius-Clapyron equation if the heat of vaporization is independent of the temperature:

$$\log P = A - B/T \quad (5)$$

But also the following empirical equation, due to Antoine, gives a very good correlation:

$$\log P = A - B/(t+C) \quad (6)$$

where t , is in degrees centigrade and P , is the pressure expressed in mm Hg. The Antoine equation is similar to equation (5), only the constant, C , in equation (5) is fixed equal to 273.16 when Kelvin temperatures are used.

Another equation derived from an approximate integration of the Clapyron equation is due to E. R. Cox (4).

$$\log P = A(1 - T_B/T) \quad (7)$$

where T_B , is the boiling point in °K, and A varies through a relatively short range and is a function of temperature. A. G. Osborn and D. R. Douslin (11) used Cox's and Antoine's equations for correlation of 36 sulfur compounds where,

$$\log A = a + bT + cT^2 \quad (8)$$

They recommended, for greater mathematical convenience the use of Antoine equation, and for greater accuracy Cox's equation.

Since Clapyron introduced his equation for relating the vapor pressure and temperature, many physicists, chemists, and chemical engineers have modified the equation. Many of these modifications

are elaborate and difficult to use. They may have as many as five or even six constants which are functions of molecular properties of the compound, such as the triple point, critical point, dipole moment, compressibility factor, etc. Partington (13) proposed a large number of equations and Miller (9) has reviewed the accuracy of such equations and critically evaluated a dozen or more "predictors" of vapor pressure data by comparing them with the experimental data.

A comparison of the different vapor pressure equations with the use of a computer by Othmer and Huang (12) showed that the simple equations are as good as any others. Thomson (20), in his review of Antoine's and other vapor pressure correlations found the Antoine equation to be extremely accurate in most instances up to a reduced temperature of 0.85. Dreisbach and Spencer (5) state that the Antoine equation is valid to $t_r = 0.95$.

Sometimes, for low vapor pressures even the simple Clausius-Clapyron equation gives adequate accuracy. As McCullough (7) and Osborn (11) comment, even though their data fit the Cox equation with more accuracy than the Antoine equation, the difference between Cox's and Antoine's equation was very small.

EXPERIMENTAL METHODS

The vapor pressure of organic compounds in the range of 0-300° C have been measured in the past by several different techniques, which are applicable to the system studied in this investigation, and are characterized by certain advantages and disadvantages.

Static Method

The static method for the determination of vapor pressures, determines pressure exerted by the vapor in equilibrium with the liquid or solid under examination at constant temperature.

In the classical method, two barometric tubes are used and are connected to the same reservoir. The substance is introduced into the torricellian vacuum of one of them. The depression of the mercury caused by the vapor pressure of the substance on one of the barometers is read by comparison to the other barometer. The method is very sensitive to the absorbed and dissolved gases, and impurities in the substance. Another objection to the method is the difficulty of obtaining reproducible measurements.

The classical static method is not recommended for vapor pressures below atmospheric pressure, however, it is applicable to high-temperature substances.

Dynamic Method

In the Boiling Point Technique for vapor pressure determination, the liquid is boiled at a finite pressure, and the temperature of the boiling liquid in equilibrium with the vapor is measured. This method is called the dynamic method and several modifications have been achieved, which have made it quite practical and accurate, however there have been many problems in using this method such as superheating, difficulties in reading the pressure, etc.

The first attempt at solving the superheating problem is due to Cottrell (3) in 1911. Cottrell placed the thermometer bulb in the gas phase and measured the condensation temperature. The Cottrell apparatus is called an ebullioscope or ebulliometer. One modification of the Cottrell ebullioscope is due to Washburn and Read (22) and a combination of the ebullioscope and the differential thermometer is due to Menzies and Wright (8). A number of other modifications have been performed by various investigators. One of these successful investigators is Swietoslowski (19), who designed the first simple ebulliometer in 1924 and developed the differential ebulliometer, with condensed vapor could be measured. An elaborate "boiling-point" apparatus has been developed by the National Bureau of Standards (23) and has been used to measure vapor pressures in the range of 47-780 mm Hg.

Compare Ebulliometer Technique

In a compare ebulliometer the boiling temperature of two liquids are compared at the same pressure.

In general this method affords the most precise vapor pressure measurement above 10 mm Hg. Its accuracy is limited only by the purity of the sample, the reference standard, and by the accuracy to which the vapor pressure of the reference standard is known.

Precise ebulliometric measurements require not only special apparatus, but also special techniques based on the comparative procedure.

In 1938, the International Union of Chemistry stated that water should be used as the primary standard, since the vapor pressure data of water is known very accurately. Thus water has been used as a reference by most investigators. A. G. Osborn and D. R. Douslin from Bartlesville Petroleum Research Center, Bureau of Mines (11) used benzene as a reference for low temperature vapor pressures.

In the experimental operation, the sample container is filled with the sample, so that there is little room for vapor, the latter phase leaves the vessel and carries some boiling liquid with it which drops to the surface of the thermometer well. Experiments have indicated that this liquid leaving the boiler is superheated. The

degrees of superheat does not ordinarily exceed 0.05°C . If Δt represents the amount of superheat, C_p the heat capacity of the liquid and Q the heat for evaporation of m gram of the liquid, the mass of the liquid m , to be evaporated in order to reach equilibrium with the vapor may be calculated by (10):

$$m = Q/C_p \Delta t \quad (9)$$

For the majority of compounds m is very small, hence equilibrium can be reached very rapidly before the liquid reaches the thermometer well.

The heat applied to the boiling liquid is regulated according to the above indication of equilibrium by a drop counter. The number of drops, n , passing the drop counter per second is proportional to the intensity of heating. There are a certain amount of drops in which the temperature does not change with the change in the number of drops per second. The intensity should be maintained, so that the number of drops should be within this range. If the number of drops is less than the lower limit, the heat is not sufficient, and if the number of drops is too large the temperature of the liquid is too high. Before each experiment the amount of drops at the equilibrium condition should be measured.

As will be discussed later, the apparatus consists of two ebulliometers, one filled with water and the other with the sample

under examination. The ebulliometers are connected through a manifold and manostat to a vacuum system. To avoid oxidation of liquid and its vapor, air in the system may be replaced by any inert gas.

The boiling temperature of the sample, t_s , at a given pressure, and the pressure under which the sample is boiling, may be determined precisely by measuring the temperature alone. The pressure can be determined by measuring the temperature of boiling water, and since t_s is a function of the pressure or, vapor pressure of the sample, thus the relationship between pressure and t_s can be established. Similarly there is a relation between t_s and the boiling temperature of water under the same pressure. This relation may be given as:

$$t_s = A + B(t_w) + C(t_w)^2 \quad (10)$$

in which A, B, and C are constants and t_w is the temperature of water. In addition:

$$(dt/dp)_s / (dt/dp)_w = \lambda \quad (11)$$

where λ , the ratio of the gradient of the boiling temperature of the substance to that of water, both produced by the same change in pressure, is a constant. In this case a precise measurement of the pressure is not required since the precise temperature measurement suffices.

This method is very accurate, easy to handle and the experimental error is small. The purity of the compound and water is the main concern. The accuracy of the method depends upon the accuracy of the temperature measurements, thus the accuracy can be increased many times over a static method under similar conditions.

APPARATUS AND EQUIPMENT

Vapor pressure measurements in this investigation were made by directly comparing the boiling temperature of the sample with the boiling temperature of water in a common pressure manifold system (Figure 1).

The differential ebulliometer (Figure 1) was based on the design described in principle by Swietoslowski (19). It consists of a boiler and condenser section where both the boiler and condenser sections have a re-entrant well for measuring the temperature of boiling liquid and condensing vapor. This differential ebulliometer, by measuring the temperature of boiling liquid and condensing vapor, has the advantage that the purity of the compound can be checked during the test, and apparatus can thus show decomposition or polymerization of the sample during the test. This helps to provide assurance that no error is introduced by contamination of the compound.

To prevent contact of the compound with the electrical heater element, the heater unit was enclosed in a glass re-entrant well in the boiler. To improve steady boiling, the inner surface of the well which was exposed to the sample, was wrapped with glass thread. Silicon fluid was used as the uniform heat transmitting medium. A brief description of the design is given as follows:

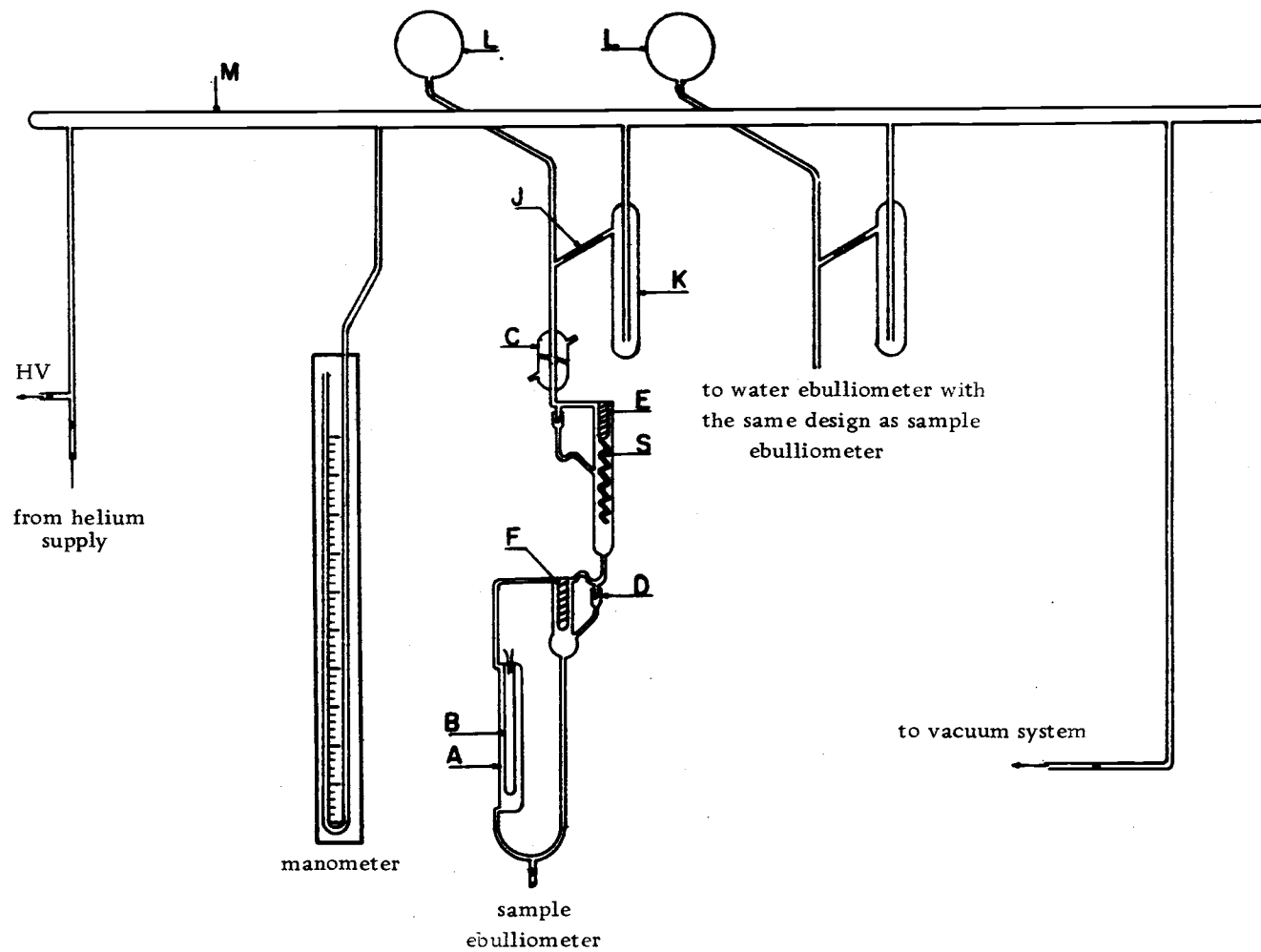


Figure 1. Experimental apparatus

The ebulliometer as shown in Figure 1 consists of a sample container (A) which has a capacity of about 80 cc; an electrical heater well (B) with glass thread covering the inner surface of the well; and electrical heater unit made from No. 32 Nickel Chromium V and mica sheet for the non-conducting part of the heater. The maximum temperature of the boiler (about 300 °C) was imposed by the design of the heater element. The boiler was connected to the temperature well by a percolator tube. This well was covered from the outside with a glass spiral, which provided better vapor contact area with the outer surface of the well and promoted better temperature distribution. The condenser temperature well (E). The glass spiral (S) was used to separate the liquid from the accompanying vapor. The rest of the apparatus consisted of drop counter (D) and a condenser (C) and a boiling temperature well (F).

The boiling and condensing temperature wells were insulated to prevent heat loss, but the percolator tube above the boiler heater and the heater unit itself remained uninsulated so that if any superheat was created in the boiling section it would be dissipated.

Each ebulliometer was connected to a manifold (Figure 1) through a diffusion barrier (J) and cooler (K). The diffusion barrier was made of glass wool to avoid any effect of the organic compound vapor on the barrier which may contaminate the sample. The condenser trap or cooler was cooled by liquid Nitrogen. The condenser

trap prevented any trace of vapor from reaching the manifold system (M). The two 12 litre flasks (L) prevented any increase of pressure in the ebulliometers during the operation, which was an important factor in this investigation.

The manifold was connected to the mercury U tube manometer, the vacuum system, the helium cylinder, and auxiliary equipment. Helium was used as the inert gas to blanket the system. The pressure of the system was controlled by a manostat.

All glass tubing, except the manifold which was 2 cm pyrex glass, was made of 7 mm pyrex glass. To avoid leaks or pollution, every connection was performed by glass blowing and the system was tested before experiment for leakage. For the same reason, all stopcocks were made of teflon.

The temperatures were measured with Copper-Constantan thermocouples. The thermometer potentials were measured with a sensitive potentiometer Type 9160 from Guildline Instruments LTD.

EXPERIMENTAL PROCEDURE

Material

Since the propylene carbonate obtained from Matheson Coleman and Bell Co. was practical grade, purification was necessary. The purification was accomplished by vacuum distillation (7 mm Hg). The sample was distilled four times for the first run of propylene carbonate. The purification technique was checked as data were collected, by determining the observed differential temperature between the boiling liquid and condensing vapor. The small difference obtained (average 0.01°C) indicated the compound was quite pure. For more assurance the sample was distilled one more time. A very small change in boiling temperature was observed and it was taken as the indication of sufficient purification.

The iso-propyl benzoate, obtained from J. T. Baker Chemical Co. was high purity grade material, and was used without any further purification.

Procedure

For each run a preliminary test was conducted to determine the equilibrium point and the condition of equilibrium. The following procedure was used:

First of all, the system was connected to a high vacuum for

cleaning purposes. Then air was replaced by helium and the sample along with the water reference was introduced to the boiler section of the ebulliometers through the inlet port at the bottom. By lowering the pressure, the system was brought to a selected pressure and maintained by vacuuming the system through a manostat. Then heating was started in the water and sample, and this was controlled by two powerstats. The temperature of the water reference was brought to an exact point by knowing the vapor pressure of water.

The amount of drops from drop counter (D) increased at this point as the heating power increased, the passing of the equilibrium point was denoted by the fact that the temperature increased as the number of drops increased. The interval during which the temperature remained constant, as the rate of addition of drops was varied, was selected as the equilibrium range. The equilibrium condition for the sample was determined by the same procedure used for water.

The equilibrium condition was determined for each compound. The results obtained are as follows:

- (1) The equilibrium condition of propylene carbonate was 90-120 drops per minute from the drop counter (D).
- (2) The equilibrium condition of iso-propyl benzoate was 110-150 drops per minute from the drop counter (D).
- (3) The equilibrium condition of water was 6-14 drops per minute from the drop counter (D).

After determining the condition of equilibrium, measurements were made along a series of pressure points. At each point the pressure of helium in the system was first adjusted approximately by the mercury manometer the boiling was initiated in the sample and water. After this the sample was brought to an equilibrium condition and the temperatures were determined by measuring the electromotive force of the thermocouples with the potentiometer. To avoid the effect of small, steady pressure drifts beyond the capability of ballast control, the temperature of water was measured again and it was taken as the final temperature of reference.

After each run the sample was removed from the system, the ebulliometer was cleaned with benzene, and before reuse it was cleaned with high vacuum.

The thermometers were calibrated at the ice point and boiling point of water as outlined by Roeser and Lonberger (15). The measured values and standard values given by Shenker et al. (18, p.35-36) are shown below:

temperature °C	emf. of thermocouple and related standard	
	measured value millivolts	standard value millivolts
0.0	0.000	0.000
100.0	4.280	4.277

And calibration was checked during the test.

The difficulty which was caused by welding of the connection of two wires of thermocouples arose during operation. The thermocouples were changed one time and were calibrated several times during the test.

Another difficulty which may have caused some errors in the data, specially for the first run of propylene carbonate was sensitivity of boiling temperature to the room temperature and wind current. To avoid it, the thermometer wells were insulated. Even with this insulation the last figure of temperatures were measured with difficulty.

Silicon fluid, which was used as the heat transmitting medium unfortunately smoked at 180°C and measurements were not able to be conducted above 232°C .

RESULTS AND CONCLUSIONS

The vapor pressure data of propylene carbonate are given in Table 1 for the first run and in Table 2 for the second run. The range of vapor pressure was from 24.8 mm Hg to 543 mm Hg for the first run and from 59 mm Hg to 620 mm Hg for the second run. Eleven different equilibrium points were measured for the first run and ten equilibrium points were measured for the second run.

The average temperature difference between two runs at a single pressure was about 0.02 °C. This small difference is indicative of the compound's high state of purity. The observed differential temperature of boiling and condensing point was between 0.01 and 0.02 °C for the first run and between 0.00 and 0.01 °C for the second run.

The plot of $\log P$ Vs. $1/T$ (with P in mm Hg and T in °K) for both runs were linear and the data can be fitted to the Clausius-Clapyron equation:

$$\log P_{\text{mm}} = A - B/T \quad (5)$$

where P is in mm Hg and T in degrees Kelvin. The constants of Clausius-Clapyron equation were determined by the method of least squares. The following equations were resulted:

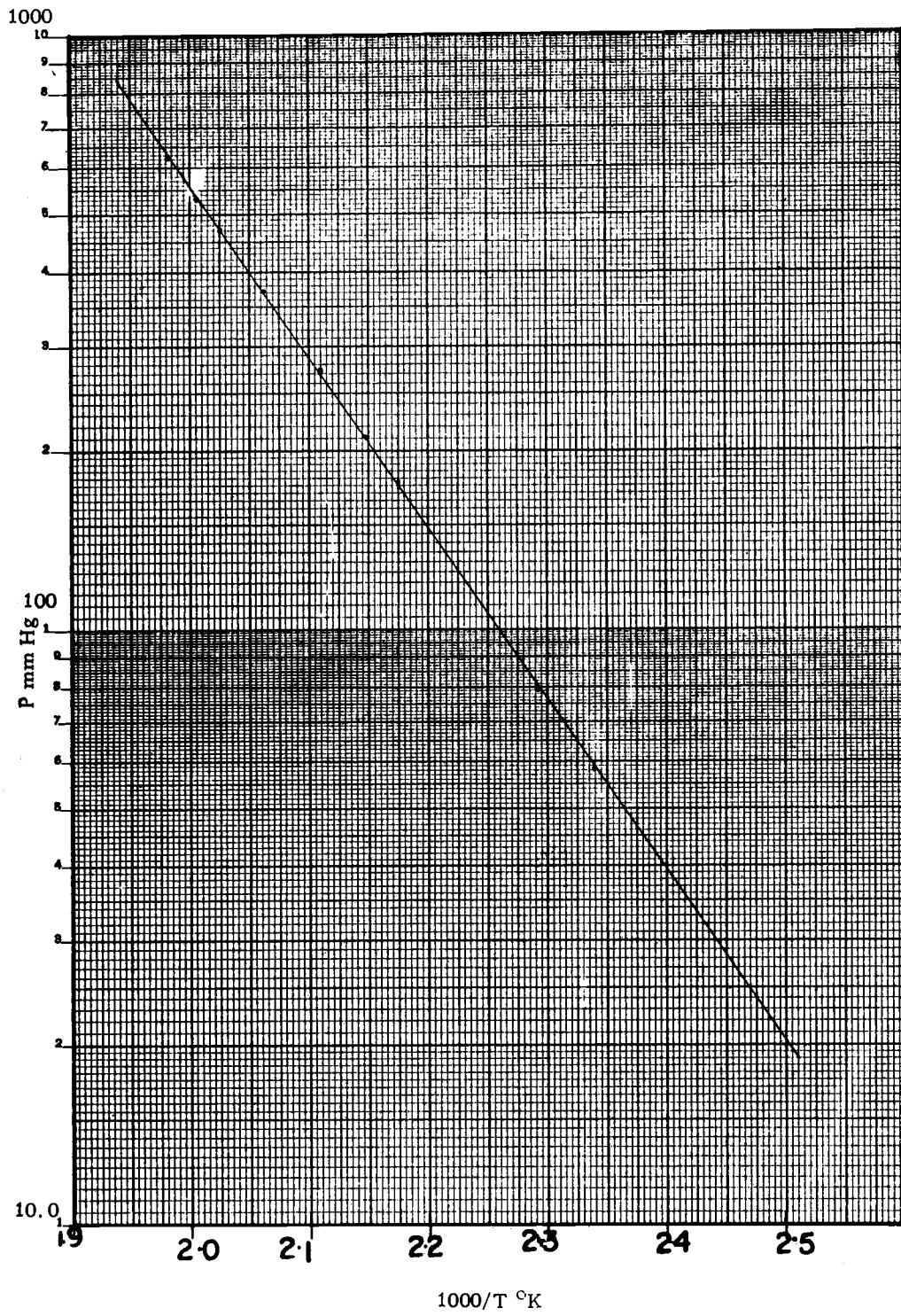


Figure 2. Plot of log P vs. 1/T for propylene carbonate

Table 1. Experimental results for propylene carbonate (run 1).

No.	P mm Hg	MV _B millivolts	t _B °C	MV _C millivolts	t _C °C	MV _w millivolts	t _w °C
1	24.8	5.802	131.85	5.801	131.84	0.999	25.27
2	30.0	6.030	136.50	6.029	136.49	1.154	29.00
3	59.0	6.906	154.03	6.905	154.01	1.661	41.21
4	80.0	7.335	162.50	7.334	162.48	1.905	47.10
5	177.0	8.575	186.53	8.574	186.52	2.635	63.71
6	210.5	8.870	192.12	8.869	192.11	2.800	67.60
7	330.0	9.700	207.70	9.699	207.69	3.277	78.20
8	370.0	9.917	211.73	9.916	211.72	3.401	81.02
9	410.2	10.124	215.55	10.123	215.54	3.519	83.60
10	470.0	10.392	220.55	10.391	220.54	3.680	87.07
11	543.0	10.688	225.99	10.687	225.97	3.852	90.85

Table 2. Experimental results for propylene carbonate (run 2).

No.	P mm Hg	MV _B millivolts	t _B °C	MV _C millivolts	t _C °C	MV _w millivolts	t _w °C
1	59.0	6.907	154.04	6.906	154.03	1.661	41.22
2	80.0	7.335	162.50	7.334	162.49	1.905	47.10
3	177.0	8.576	186.55	8.576	186.55	2.635	63.71
4	210.5	8.873	192.19	8.872	192.18	2.800	67.58
5	270.2	9.321	200.60	9.320	200.59	3.059	73.40
6	370.0	9.918	211.75	9.917	211.74	3.401	81.00
7	410.2	10.127	215.61	10.126	215.60	3.519	83.60
8	470.0	10.393	220.56	10.392	220.55	3.680	87.07
9	543.0	10.689	226.00	10.688	225.99	3.852	90.85
10	620.0	10.985	231.40	10.984	231.39	4.018	94.40

$$\log P_{\text{mm}} = 8.50014 - 2876.151/T \quad (12)$$

for the first run and:

$$\log P_{\text{mm}} = 8.44057 - 2847.96/T \quad (13)$$

for the second run.

For comparison the measured and calculated values are tabulated in Table 3 for the first run and in Table 4 for the second run. The deviations are from -0.28 to 0.35 °C for the first run and from -0.34 to $+0.21$ °C for the second run. The deviations are rather large and indicative of the poor agreement between experimental data and Clausius-Clapyron equation.

The observed difference between determined constants of the Clausius-Clapyron equation for the two runs of propylene carbonate were indicative of the boiling temperature difference for the two runs. These boiling temperature differences were between 0.01 and 0.07 °C and were caused by less purity of compound in the first run and by random errors in the measurement for the first run. Higher purity of compound and taking advantage of experiences from the first run, caused the improvement in the accuracy of collected data for the second run.

The large deviations for both runs between the measured and calculated values indicate that, the heat of vaporization of propylene carbonate depends on the boiling temperature.

Table 3. Comparing calculated values from the Antoine and Clausius-Clapyron correlations for propylene carbonate (run 1) with the experimental data.

mm Hg	t_B °C	t_{An} °C	$t_{An}-t_B$ °C	t_{C-C} °C	$t_{C-C}-t_B$ °C
24.8	131.85	131.85	0.00	131.61	-0.24
30.0	136.50	136.53	+0.03	136.41	-0.09
59.0	154.03	154.01	-0.02	154.25	+0.22
80.0	162.50	162.48	-0.02	162.81	+0.31
177.0	186.53	186.49	-0.04	186.86	+0.33
210.5	192.12	192.14	+0.02	192.47	+0.35
330.0	207.70	207.57	-0.13	207.67	-0.03
370.0	211.73	211.69	-0.04	211.70	-0.03
410.2	215.55	215.46	-0.09	215.39	-0.16
470.0	220.55	220.55	+0.00	220.34	-0.21
543.0	225.99	226.08	+0.18	225.71	-0.28
760.0	--	239.52			

Table 4. Comparing calculated values from the Antoine and the Clausius-Clapyron equations for propylene carbonate (run 2), with the experimental data.

P mm Hg	t_B °C	t_{An} °C	$t_{An}-t_B$ °C	t_{C-C} °C	$t_{C-C}-t_B$ °C
59.0	154.04	154.04	0.00	153.92	-0.18
80.0	162.50	162.51	+0.01	162.47	-0.03
177.0	186.55	186.53	-0.02	186.74	+0.19
210.5	192.19	192.18	-0.01	192.40	+0.21
270.2	200.60	200.62	+0.02	200.80	+0.02
370.0	211.75	211.73	-0.02	211.81	+0.06
410.2	215.61	215.51	-0.10	215.54	-0.07
470.0	220.56	220.60	+0.04	220.55	-0.01
543.0	226.00	226.13	+0.13	225.98	-0.02
620.0	231.40	231.34	-0.06	231.06	-0.34
760.0	--	239.57			

Then the data were fitted to the Antoine equation given below:

$$\log P_{\text{mm}} = A - B/(t+C) \quad (6)$$

The curve fitting was done by the method of least squares as outlined by Scarborough (17) and resulted in the following equation:

$$\log P_{\text{mm}} = 7.69154 - 2194.20/(t+216.59) \quad (14)$$

for the first run and:

$$\log P_{\text{mm}} = 7.69396 - 2196.67/(t+216.82) \quad (15)$$

for the second run.

The calculated values by the Antoine equation are tabulated in Table 3 for the first run and in Table 4 for the second run. The experimental data fit the Antoine equation quite well, with the second run showing a better agreement than the first one. The maximum deviation in the boiling temperatures observed by using the Antoine equation was on the order of 0.08 percent for the first run and 0.06 percent for the second run, which support the indication of accuracy of the second run and better agreement of the second run with the Antoine equation. As was mentioned in the procedure section, because only a poor heat transmitting fluid was available, it was not possible to collect data for atmospheric pressure. However, by using equations (14) and (15) and extrapolation to 760 mm Hg pressure boiling point of propylene carbonate was found to be 239.52°C

for the first run and 239.57°C for the second run. These values agreed quantitatively with the value of 240°C reported in Handbook of Chemistry and Physics (2).

The vapor pressure data of iso-propyl benzoate were collected for ten different equilibrium points and are given in Table 5. The pressure range was from 56.2 mm Hg to 760 mm Hg. The difference between the boiling temperature and condensing temperature was between 0.00 and 0.01°C.

The plot of $\log P$ vs. $1/T$ was nearly linear and curve fitting by using the Clausius-Clapyron equation resulted in the following equation:

$$\log P = 8.16608 - 2597.69/T \quad (16)$$

The deviations calculated by using the above equation were between -0.20 and +0.23°C. The numerical analysis of the data by using the Antoine equation resulted in the following equation:

$$\log P = 7.62267 - 2132.68/(t+231.23) \quad (17)$$

The maximum deviation from the experimental data was 0.03 percent and excellent agreement between the data and the Antoine equation was observed. The comparison between experimental data and calculated data values is shown in Table 6.

There is no previously published vapor pressure data for comparison with the experimental data in this work. However the boiling point of iso-propyl benzoate at atmospheric pressure has been

Table 5. Experimental data for isopropyl benzoate.

No.	P mm Hg	MV _B millivolts	t _B °C	MV _C millivolts	t _C °C	MV _w millivolts	t _w °C
1	56.2	5.805	131.90	5.805	131.90	1.622	40.30
2	96.0	6.550	146.90	6.550	146.90	2.067	50.74
3	174.5	7.468	165.10	7.467	165.09	2.617	63.40
4	270.2	8.218	179.64	8.217	179.63	3.059	73.40
5	370.0	8.793	190.66	8.787	196.65	3.401	81.02
6	465.1	9.247	199.20	9.246	199.19	3.659	86.80
7	564.0	9.640	206.56	9.640	206.56	3.898	91.86
8	641.5	9.914	211.67	9.913	211.66	4.060	95.32
9	730.6	10.197	216.95	10.197	216.95	4.226	98.88
10	760.0	10.282	218.49	10.281	218.48	4.277	100.0

Table 6. Comparing calculated values from the Antoine and the Clausius-Clapyron correlations for iso-propyl benzoate, with the experimental data.

P mm Hg	t_B °C	t_{An} °C	$t_{An}-t_B$ °C	t_{C-C} °C	$t_{C-C}-t_B$ °C
56.2	131.90	131.90	+0.00	131.70	-0.20
96.0	146.90	146.87	-0.03	146.92	+0.02
174.5	165.10	165.11	+0.01	165.32	+0.22
270.2	179.64	179.61	-0.03	179.84	+0.02
370.0	190.66	190.70	+0.04	190.89	+0.23
465.1	199.20	199.16	-0.04	199.28	+0.08
564.0	206.56	206.56	+0.00	206.58	+0.02
641.5	211.67	211.65	-0.02	211.59	-0.08
730.6	216.95	216.90	-0.05	216.75	-0.20
760.0	218.49	218.52	+0.03	218.34	-0.15

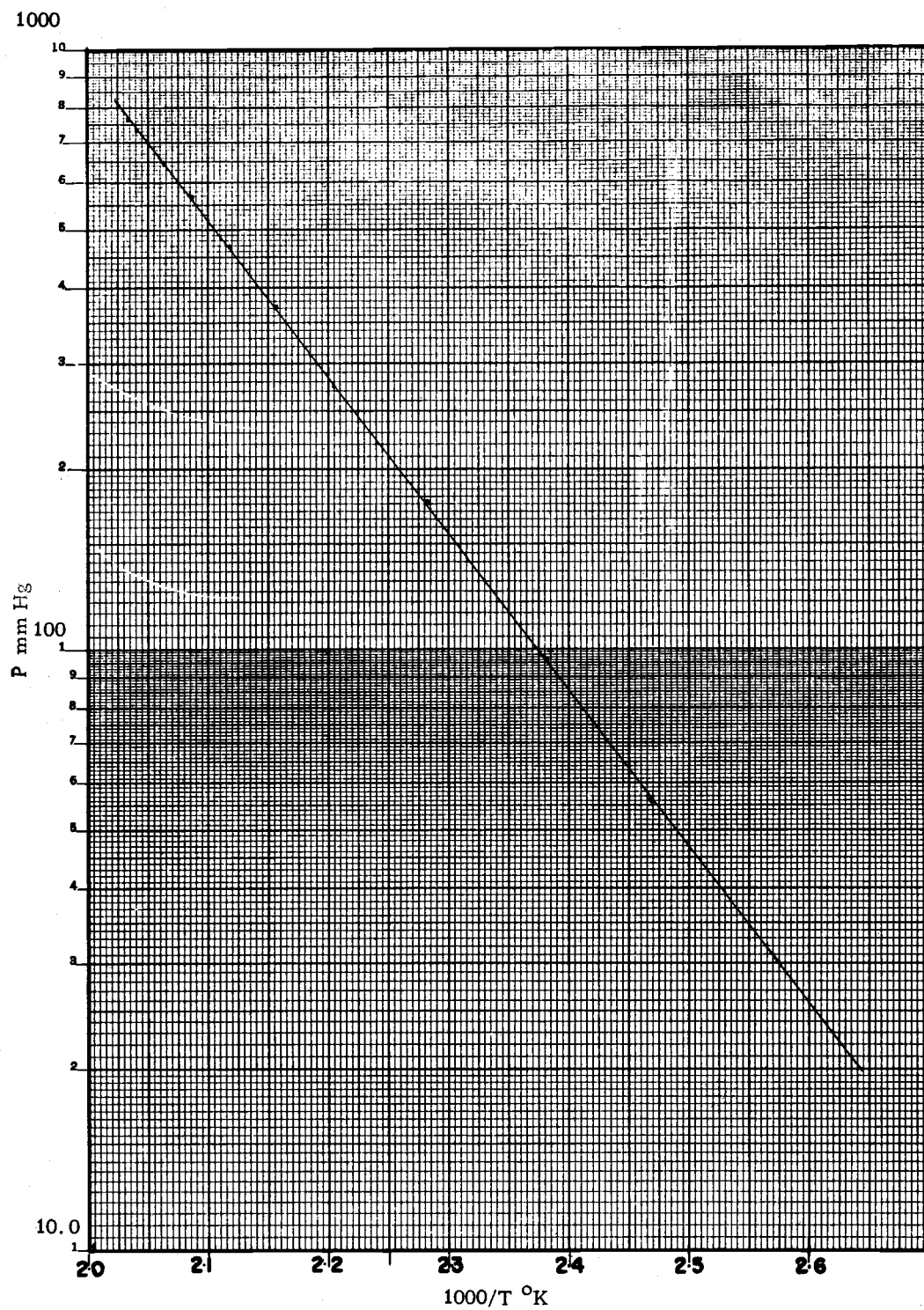


Figure 3. Plot of log P vs. 1/T for iso-propyl benzoate

previously reported to be 218.5°C, which agrees quite well with the measured value of 218.49°C in this work. The boiling point of propylene carbonate has been reported to be 232.5°C by Walker (21), 241.7°C by Peppel (14) and 240°C by R. C. Weast (2). The first value is far off from the other two and the value was calculated in this work by using the Antoine correlation for the second run of propylene carbonate. The last value agrees quite well with the calculated value in this investigation.

Overall, it was concluded, that the experimental data of both compounds are in excellent agreement with the Antoine correlations. The second run of propylene carbonate is more accurate than the first run. The two equations, (15) and (17) represent the experimental data in this work quite well and are recommended for use.

The accuracy of vapor pressure data were determined using the Clapyron equation (10) :

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T \Delta V} \quad (1)$$

where ΔH is the heat of vaporization of water in cal/gr, ΔV is the specific volume of evaporation in cm^3/gr , T is the temperature in degrees Kelvin, ΔT is the temperature inaccuracy in degrees Kelvin and ΔP is the error in pressure expressed in mm Hg.

The temperatures have been derived from the "Reference Tables for Thermocouples" by Sherker et al. (18). The observed emfs. of

the thermocouples in this investigation were converted to the emfs. of standard table, using the correction values for the thermocouples in this investigation. The correction values were determined by plotting ΔE vs. E_{obs} at the calibration points where $\Delta E = E_{obs.} - E_{stan.}$. Here E_{obs} is the measured value of the emf. and E_{stan} is emf. from the standard tables for the same temperature. Roserer and Dahl (16) showed that for Cooper-Constantan thermocouples the plot of ΔE vs. $E_{obs.}$ is linear and there is no significant error in using the standard tables and taking into account the linear deviation of $E_{obs.}$ from $E_{stan.}$

Because the deviation for each thermocouples was different a plot of ΔE vs. $E_{obs.}$ was prepared separately for each thermocouple. The correction values for each measured point were then determined and the measured emf. values were converted to $E_{stan.}$ by the relationship $E_{stan.} = E_{obs.} - \Delta E$. All temperatures were derived from the Shenker's table, using the above calculated $E_{stan.}$.

It was not possible to determine precisely the temperature accuracy in this investigation because Shenker (18) did not give any accuracy for his table from which the temperatures for this investigation were derived. However, Shenker's table was derived from Adam's table (1) which has an accuracy of one hundredth of a degree centigrade. The maximum temperature inaccuracy was determined roughly to be in the order of $\pm 0.03^{\circ}\text{C}$. This value was determined

by examination of the method used by Shenker to derive the values for his table from Adam's table. Estimating the error of Shenker's values plus estimating the error present in assuming a linear relationship in the plot of ΔE vs. E_{obs} , one obtains the above figure.

A sample calculation for the evaluation of the inaccuracy in the reported vapor pressure data which arises from the inaccuracy of the measured temperature of water is given below. The data for water were taken from the data reported by Keenan and Keyes (6).

At the boiling point of water:

$$P = 760 \text{ mm Hg}$$

$$T = 373.16 \text{ }^\circ\text{K}$$

$$\Delta H = 970.2 \text{ Btu/lb.}$$

$$\Delta V = 26.8 \text{ ft.}^3/\text{lb.}$$

$$\text{for } \Delta T = 0.03 \text{ }^\circ\text{K}$$

then

$$\Delta P = \frac{970.2 \frac{\text{Btu}}{\text{lb.}} \cdot 778.16 \frac{\text{ft. lb.}_f}{\text{Btu}} \cdot 0.35913 \frac{\text{mm Hg}}{\text{lb.}_f \text{ft.}^{-2}} \cdot 0.03^\circ\text{K}}{373.16^\circ\text{K} \times 26.8 \frac{\text{ft.}^3}{\text{lb.}}}$$

$$\Delta P = 0.9 \text{ mm Hg.}$$

$$\text{percent error} = \frac{0.9 \times 100}{760} = 0.12 \%$$

The errors for different points were determined in the same manner and the maximum relative error of vapor pressure data was found to be of the order of 0.15%.

MATHEMATICAL ANALYSIS OF DATA

In order to obtain a correlation for the collected data the Clausius-Clapyron equation:

$$\log P = A - B/T \quad (18)$$

and the Antoine equation

$$\log P = D - E/(t+C) \quad (19)$$

were used. In the above, T represents temperature in Kelvin degrees, t represents temperature in centigrade degrees and P denotes pressure in mm Hg.

The Evaluation of the Clausius-Clapyron Equation for Iso-Propyl Benzoate

In equation(18) let $X = 1/T$ and $Y = \log P$. If N represents the number of data points, then A and B can be found by using the method of least squares. Putting in equation (18), for $1/T$ and $\log P$ respected notes therefore,

$$Y = A - BX$$

then

$$\begin{aligned} \Sigma Y &= AN - B\Sigma X \\ \Sigma XY &= A\Sigma X - B\Sigma X^2 \end{aligned} \quad (20)$$

Solving the above simultaneous equations give:

$$A = \Sigma Y/N - B (\Sigma X/N)$$

$$B = (\Sigma XY - \Sigma X \Sigma Y/N) / (\Sigma X^2 - (\Sigma X)^2/N)$$

The calculated values for X, Y, XY, and X² are given in Table 7.

Table 7. Numerical values for evaluation of Clausius-Clapyron equation for iso-propyl benzoate.

No.	P	X10 ³	Y	XY10 ³	X ² 10 ⁶
1	56.2	2.4688	1.7497	4.3197	6.0948
2	96.0	2.3806	1.9823	4.7190	5.6672
3	174.5	2.2818	2.2418	5.1153	5.2065
4	270.2	2.2085	2.4317	5.3703	4.8773
5	370.0	2.1560	2.5682	5.5371	4.6484
6	465.1	2.1170	2.6675	5.6473	4.4818
7	564.0	2.0845	2.7513	5.7351	4.3453
8	641.5	2.0626	2.8072	5.7900	4.2542
9	730.6	2.0403	2.8637	5.8429	4.1630
10	760.0	2.0340	2.8808	5.8595	4.1371

Putting back the calculated values into equations (20) yields:

$$24.9442 = 10A - 0.021834 B$$

$$53.9363 \times 10^{-3} = 21.834 \times 10^{-3} A - 0.047875 \times 10^{-3} B$$

The solution of the above equations give:

$$A = 8.16608$$

$$B = 2597.69$$

Therefore the Clausius-Clapyron equation of iso-propyl benzoate is:

$$\log P = 8.16608 - 2597.69/T$$

The calculations for propylene carbonate were carried out in an analogous manner.

The Evaluation of the Antoine Equation for Iso-Propyl Benzoate

The least squares method as outlined by the J. B. Scarborough (17, p. 545-547) was used to evaluate the constants of Antoine equation.

Initially, the approximate values of the constants D, E, and C in equation (19) were calculated. These approximate values were designated as S, M, and K respectively. Putting S, M, and K values in equation (19) instead of D, E, and C, the approximate value of log P related to temperature t can be calculated:

$$Y = S - M/(t+K) \quad (21)$$

where Y represents the approximate values of log P. The determined values of S, M, and K were:

$$S = 7.60135$$

$$M = 2114.65$$

$$K = 229.75$$

then

$$Y = 7.60135 - 2114.65/(t+229.75) \quad (22)$$

The partial derivatives of Y (equation 21) with respect to S, M, and K are

$$\partial Y / \partial S = 1$$

$$\partial Y / \partial M = -1/(t+K)$$

$$\partial Y / \partial K = M/(t+K)^2$$

and r, the deviation between real and approximate value of log P is

$$r = \log P - Y$$

The partial derivatives and r are given in Table 8.

If the difference between D and S, E and M, and C and K are represented by α , β , and γ respectively:

$$\alpha = D - S$$

$$\beta = E - M$$

$$\gamma = C - K$$

then V can be evaluated at each data point, where V is:

$$V = (\partial Y / \partial S)\alpha + (\partial Y / \partial M)\beta + (\partial Y / \partial K)\gamma + r.$$

The ΣV , as well as ΣtV and $\Sigma t^2 V$ given below have to be zero:

$$\Sigma V = \alpha \Sigma \partial Y / \partial S + \beta \Sigma \partial Y / \partial M + \gamma \Sigma \partial Y / \partial K + \Sigma r = 0$$

$$\Sigma tV = \alpha \Sigma t \partial Y / \partial S + \beta \Sigma t \partial Y / \partial M + \gamma \Sigma t \partial Y / \partial K + \Sigma tr = 0$$

$$\Sigma t^2 V = \alpha \Sigma t^2 \partial Y / \partial S + \beta \Sigma t^2 \partial Y / \partial M + \gamma \Sigma t^2 \partial Y / \partial K + \Sigma t^2 r = 0$$

The calculated values for $\partial Y/\partial S$, $\partial Y/\partial M$, $\partial Y/\partial K$, and r along with their values multiplied by t and t^2 are tabulated in Table 8.

$$\Sigma V = 10a - 0.024132\beta + 0.12379\gamma + 0.03808 = 0$$

$$\Sigma tV = 1867.07a - 4.4556\beta + 22.589\gamma + 6.9861 = 0$$

$$\Sigma t^2V = 356813a - 843.39\beta + 4232.2\gamma + 1314.5 = 0$$

The solution of these three simultaneous equations gives a , β , and γ

$$a = 0.02132$$

$$\beta = 18.03$$

$$\gamma = 1.48$$

The values of D , E , and C can be obtained:

$$D = 7.60135 + 0.02132 = 7.62267$$

$$E = 2114.65 + 18.03 = 2132.68$$

$$C = 229.75 + 1.48 = 231.23$$

Therefore the final form of the Antoine equation for iso-propyl benzoate is:

$$\log P = 7.62267 - 2132.68/(t + 231.23)$$

The calculations for propylene carbonate were carried out in an analogous manner.

Table 8. Numerical values for evaluation of Antoine equation for iso-propyl benzoate.

No.	P mm Hg	$^{\circ}\text{C}$	$\frac{\partial Y}{\partial S}$	$\frac{\partial Y}{\partial M} 10^3$	$\frac{\partial Y}{\partial K} 10^3$	r	$t \frac{\partial Y}{\partial S}$	$-t \frac{\partial Y}{\partial M}$	$t \frac{\partial Y}{\partial K}$	tr	$t^2 \frac{\partial Y}{\partial S}$	$-t^2 \frac{\partial Y}{\partial M}$	$t^2 \frac{\partial Y}{\partial K}$	$t^2 r$
1	56.2	131.90	1	2.76509	16.1681	0.00440	131.90	0.36472	2.13259	0.58037	17398.1	48.107	281.29	76.552
2	96.0	146.90	1	2.65497	14.9058	0.00476	146.90	0.39002	2.18970	0.69925	21580.2	57.295	321.67	102.722
3	174.5	165.10	1	2.53264	13.5639	0.00390	165.10	0.41813	2.23934	0.64387	27256.4	69.030	369.70	106.300
4	270.2	179.64	1	2.44264	12.6170	0.00434	179.64	0.43880	2.26656	0.77965	32272.0	78.829	407.17	140.059
5	370.0	190.66	1	2.37865	11.9646	0.00314	190.66	0.45351	2.28114	0.59866	36350.1	86.464	434.91	114.139
6	465.1	199.20	1	2.33127	11.4927	0.00398	199.20	0.46439	2.28936	0.79282	39680.6	92.506	456.04	157.930
7	564.0	206.56	1	2.29193	11.1081	0.00344	206.56	0.47343	2.29452	0.71058	42668.3	97.793	473.96	146.779
8	641.5	211.67	1	2.26542	10.8526	0.00359	211.67	0.47952	2.29717	0.75989	44804.2	101.500	486.24	160.846
9	730.6	216.95	1	2.23864	10.5974	0.00372	216.95	0.48567	2.29911	0.80705	47067.3	105.367	498.79	175.089
10	760.0	218.49	1	2.23097	10.5251	0.00281	218.49	0.48743	2.29958	0.61394	47735.7	106.497	502.42	134.137

NOMENCLATURE

<u>Symbol</u>	<u>Definition</u>	<u>Units</u>
Mv_B	Emf. of boiling temperature of sample thermocouple	Millivolts
Mv_C	Emf. of condensing temperature of sample thermocouple	Millivolts
Mv_w	Emf. of boiling temperature of water thermocouple	Millivolts
P	Vapor pressure of sample	mm Hg
t_B, t	Boiling temperature of sample	$^{\circ}C$
t_C	Condensing temperature of sample	$^{\circ}C$
$t_{An.}$	Boiling temperature of sample calculated by using the Antoine equation	$^{\circ}C$
$t_{An.} - t_B$	Deviation of experimental data from the Antoine equation	$^{\circ}C$
t_{C-C}	Boiling temperature of sample calculated by using the Clausius-Clapyron equation	$^{\circ}C$
$t_{C-C} - t_B$	Deviation of experimental data from the Clausius-Clapyron equation	$^{\circ}C$
T_B	Boiling temperature of sample at 760 mm Hg pressure	$^{\circ}K$
T	Boiling temperature of sample	$^{\circ}K$

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