Calorimetric Determination of the Isothermal Pressure Effect on the Enthalpy of the Propane-Benzene System

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An isothermal throttling calorimeter system has been built for obtaining the effects of pressure on the enthalpy of liquids and vapors. The propane-benzene system has been studied at 200°, 300°, and 400°F. for pressures from 200 to 1,000 lb./sq.in.abs.

The experimental results are evaluated with respect to errors, and the data on the pure components are compared with values from the literature. Calculation methods are employed, and the calculated results are compared with the experimental data in an effort to evaluate the calculation methods.

Enthalpies are required for economic evaluation and design of chemical and physical processes. Accurate enthalpy data would allow an engineer to make a much better design than he could make without them. Enthalpy ignorance often results in more costly or less efficient process plants.

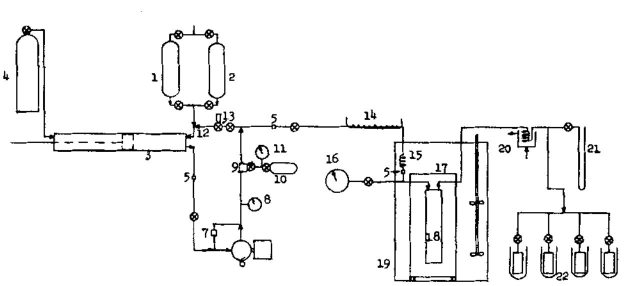
Very few experimentally measured enthalpy data exist, especially for mixtures. Most of the enthalpy data that are available in the literature have been calculated from pressure-volume-temperature data. Thus, a great void exists in the literature in the field of experimental enthalpy measurements which needs to be filled. Experimental data could be used to prove or to develop improved enthalpy correlations or calculation methods.

All types of enthalpy data, enthalpies of liquids and vapors and the heat of vaporization for pure components and mixtures, are needed. This paper describes an apparatus which was constructed to measure for liquid and vapor mixtures, and pures, the isothermal pressure effect on the enthalpy (that is, enthalpy difference between a given pressure and zero pressure, both at same temperature). Thus, the ideal gas state, where heats of mixing are negligible, is the basis for the experimental measurements. The ideal gas state enthalpies (*2*) are combined with the experimental data to give a complete enthalpy network for any substance or mixture.

The isothermal throttling calorimeter used was an integral type, so-named because the calorimeter caused large pressure drops which allowed the enthalpy difference to be measured directly, as contrasted to the differential calorimeter, in which measurements are made for small pressure drops. The integral type of calorimeter is quite versatile in that enthalpy measurements can be made for coexisting vapor-liquid systems, while only single-phase data can be measured with the differential type calorimeter.

The first integral type of isothermal throttling calorimeter was described by Gilliland and Lukes (*11*) and was later used by Gilliland and Parekh (*12*). The calorimeter used in this work is similar, with modifications.

Experimental data were measured for the propane-benzene system for which phase equilibria data are available (*13*). The pure component enthalpy results were compared with enthalpies given in the literature. Mixture and pure component enthalpy data were compared with various enthalpy calculation methods, thus evaluating the calculation methods.



1. Benzene Reservoir} Benzene-Propane
2. Propane Reservoir} Mixture Reservoirs
3. Constant Pressure Charge Cylinder
4. Nitrogen for Charge Cylinder
5. Micron Filter
6. Charge Pump
7. Rupture Disk
8. Pump Outlet Pressure Gauge
9. Mity Mite Pressure Regulator
10. Nitrogen for Pressure Regulator
11. Mity Mite Dome Pressure Gauge
12. Recycle Line
13. Metering Valve to Split Flow
14. Preheater
15. Inlet Temperature Equilibration Coil
16. Inlet Pressure Gauge
17. Stagnant Air Bath Immersed in Oil Bath
18. Calorimeter in Vacuum Jacket
19. Constant Temperature Oil Bath
20. Water Cooler
21. Outlet Pressure Manometer
22. Flow Collection Bombs in Dewars

Fig. 1. Schematic diagram of equilibrium apparatus.

EXPERIMENTAL APPARATUS

A schematic flow diagram of the apparatus is shown in Figure 1. Feed stocks (pure components or mixtures) were held in the reservoir cylinders 1 and 2. During a run, the fluid was pushed from one of the reservoir cylinders into the constant pressure charge cylinder, 3, which was a piston-cylinder arrangement which assured that a subcooled liquid was fed to the diaphragm charge pump, 6. The pulsations of the charge pump were damped by the gas loaded pressure regulator, 9. After leaving the pressure regulator, 9, the fluid could either be recycled to the charge cylinder or be sent to the calorimeter. Before entering the calorimeter, the fluid was preheated 14, tempered, 15, and the inlet pressure was measured, 16. Upon leaving the calorimeter, 18, calorimeter holder, 17, and the temperature bath, 19, the fluid was quenched, 20, the outlet pressure measured, 21, and the fluid was collected in aluminum bombs, 22. The amount collected was determined by weighing.

The charge pump used was a diaphragm laboratory feed pump. The pump had a variable piston stroke length which was used to control the flow to the calorimeter. The pressure regulator on the pump outlet was a gas dome loaded regulator. The inlet pressure gauge was a 16 in. 3,000 lb./sq. in. gauge which was calibrated. The pressure could be read to the nearest pound per square inch.

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An oil bath thermostat, 19, controlled by a thermotrol with a platinum resistance thermometer sensing element was used in maintaining a uniform temperature around the calorimeter container. The thermotrol could be used as an on-off, proportional, or proportional-reset controller. Thermocouples, which were used to measure temperature, were calibrated with a platinum resistance thermometer.

A potentiometer was used to measure the thermocouple electromotive forces and the electromotive forces of the standard resistors in the series-parallel energy circuit. A reversing switch was used to reverse the circuit which accounted for any stray electromotive forces. The power supply could be continuously varied from 0 to 5 amp. and 0 to 75 v.

Calorimeter

Details of the calorimeter are shown in Figure 2. When in use, it was placed in a stagnant air bath which was immersed in the oil bath. The inside wall of the air bath was covered with aluminum foil. Thus, when the calorimeter and bath temperatures were equal, no heat transfer would occur between the calorimeter and its surroundings.

The fluid entered the calorimeter inlet stagnation chamber, 2, at the temperature of the oil bath and impinged on the inlet thermowell, 5. The fluid then flowed through the tubing coupling, 10, and into the coiled stainless steel capillary, 18. The capillary (0.022 in. I.D. × 0.00525 in. wall × 80 in. long) was used for pressure drop and as a heater. The fluid left the end of the capillary, held down by set screw, 20, and expanded into the calorimeter volume. The fluid then passed back over the outside of the capillary where it picked up more heat, turned down between cylindrical baffles 14 and 15, and passed between the outside wall, 9, and baffle 14 to the outlet stagnation chamber, 3. There the outlet temperature was measured before the fluid left the calorimeter.

The teflon insulated electrical leads, 6, were sealed into the calorimeter cap by compression fittings. One lead, 23, connected to the capillary anchor, 19, which was insulated from the calorimeter. The other lead connected to the brass ring, 11, opposite set screw, 12. The silvered glass tube, 16, kept the capillary from shorting as well as being a radiation shield.

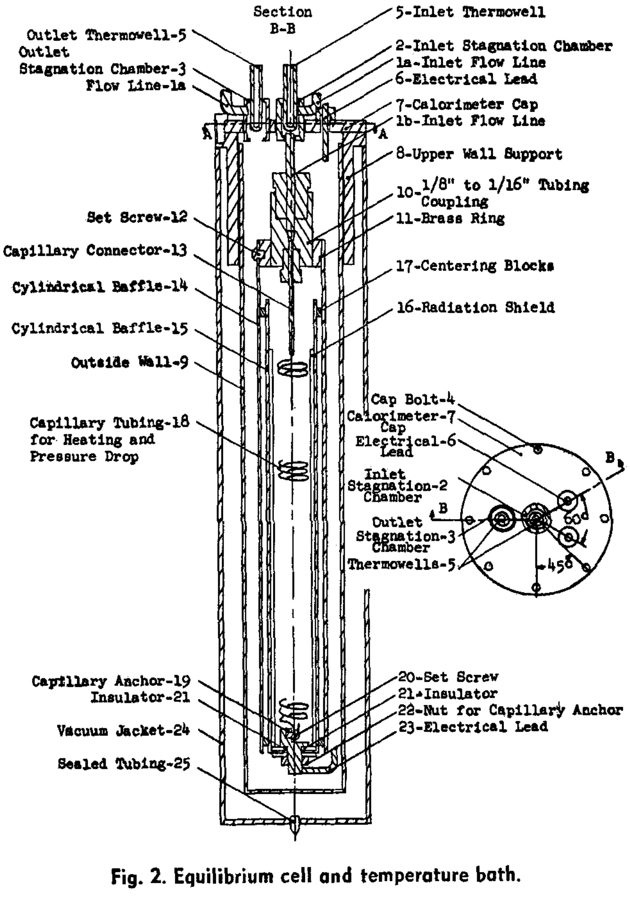

Fig. 2. Equilibrium cell and temperature bath.

In addition to the silvered glass radiation shield, the outside of baffle 14, the inside of the wall, 9, and the outside of the vacuum jacket, 24, were kept polished. Before the vacuum jacket was placed around the calorimeter body, the outside of the wall, 9, and the inside of the vacuum jacket, 24, were polished. The volume between the vacuum jacket and the calorimeter was evacuated to a pressure of 5μ of mercury, and the tubing, 25, was closed.

Thermocouples were placed along the side of the calorimeter vacuum jacket as well as in the inlet and outlet thermowells. During operation the calorimeter skin temperature was very nearly isothermal; temperature gradients along the calorimeter were on the order of a few hundredths of a degree.

The calorimeter volume was held at the low outlet pressure by the condensing temperature of the collection bomb. The condensing bath surrounding the collection bomb was dry ice and iso-octane for propane and the propane-benzene mixtures and was ice and water for benzene.

The outside diameter of the calorimeter was 2¼ in., and the overall length was about 11 in. Construction details for both the calorimeter and the components in Figure 1 are given by Yarborough (*31*).

Materials

The propane and benzene were pure grade chemicals (99 mole % minimum). The impurities were checked by chromatography. The chromatograph used was a hydrogen flame ionization detector which detected only hydrocarbons. The hydrocarbon impurity found in benzene was less than 0.5 mole %, and is probably toluene. Two traces of hydrocarbon impurities were noted in propane of which the total impurity would be less than 0.2 mole %. However, neither nitrogen nor carbon dioxide impurity could be checked.

EXPERIMENTAL PROCEDURE

The experimental procedure was basically a trial and error one. Once the run variables, temperature, inlet pressure, and fluid composition had been set, the relation of the calorimeter outlet temperature to the inlet temperature dictated the power supply setting. Usually the method of bracketing the correct power setting was used. From 45 to 180 min. were required to line-out the apparatus and reach steady operation. This depended on the flow rate and how good the initial power estimate was. The run time varied from 15 to 45 min., but generally was about 30 min.

The calorimeter was designed so that no useful work was done, no potential energy changes occurred, and kinetic energy changes were negligible in the calorimeter. Thus, the first law of thermodynamics steady state flow equation requires that the heat put into the system equals the enthalpy change between the inlet and outlet conditions. When the inlet and outlet temperatures are identical, the isothermal pressure effect on the enthalpy of the fluid being run can be obtained directly when the outlet pressure is zero. A small enthalpy correction is required to place the experimental data on ideal gas state basis (zero pressure). The small enthalpy correction at the outlet pressure was calculated via the virial equation of state.

In several runs the inlet or outlet temperatures were a few tenths of a degree from the run temperature desired. In these cases heat capacities were used to correct the experimental data. The corrections were always small, rarely totaling 0.5 B.t.u./lb.

EXPERIMENTAL RESULTS

Experimental results are listed in Table 1. The experimental data were taken for both pure components and three mixtures at 200°, 300°, and 400°F. for pressures from 200 to 1,000 lb./sq. in. abs. For the mixtures, data were taken just above the bubble-point pressure, just below the dew-point pressure, and in the two-phase region whenever possible. Phase behavior data were available for the propane-benzene binary system (*16*) in the temperature range of interest.

A plot of the enthalpy difference against composition would give an indication of mixing effects for the propane-benzene system. Such a plot was made for 400°F. and 200 lb./sq. in. abs., when both pure components are in the gaseous state. A straight line could be drawn through the data which indicates that there are no appreciable heat effects on mixing the two gases at these conditions.

Figure 3 was drawn on the assumption that the enthalpy difference is constant with pressure for liquid benzene at 200°F. Figure 3 is at conditions (200°F. and 750 lb./sq. in. abs.) where both the pure components are liquids, and propane is quite close to its critical temperature. The data show that there is a definite heat effect when these two liquids are mixed at constant temperature and pressure.

A different type of plot is shown in Figure 4. At these conditions (400°F. and 1,000 lb./sq. in. abs.) pure benzene is a liquid and pure propane is a gas. The pressure, 1,000 lb./sq. in. abs., is above the maximum critical pressure of the binary which allows a continuous curve to be drawn from pure benzene to pure propane. At 400°F. and 1,000 lb./sq. in. abs., the 25.2 mole % propane mixture is a liquid, the 49.8 mole % propane mixture is very close to its critical temperature (a dense fluid), and the 79.7 mole % propane mixture is in the gaseous state. The heat effects in the gas and liquid states are opposite, which causes the S shaped curve in Figure 4.

TABLE 1. EXPERIMENTAL RESULTS

Run No.	Temp., °F.	Pressure, lb./sq. in. abs.	Phase	Δh, B.t.u./lb.
		Pure propane		
3	200	200	V	−11.51
8	200	200	V	−11.79
2	200	500	V	−44.15
4	200	500	V	−43.96
7	200	500	V	−42.49
14	200	500	V	−44.83
15	200	500	V	−43.98
119	200	500	V	−43.80
9	200	560	V	−58.76
10	200	560	V	−58.25
12	200	600	L	−117.38
13	200	600	L	−115.10
31	200	750	L	−124.29
19	300	200	V	−7.39
20	300	200	V	−8.66
17	300	500	V	−21.48
18	300	500	V	−24.26
120	300	500	V	−21.91
16	300	750	V	−41.37
21	300	750	V	−39.83
27	300	1,000	V	−63.03
25	400	200	V	−6.66
24	400	500	V	−17.94
22	400	750	V	−27.64
26	400	1,000	V	−37.68
		Pure benzene		
58	200	500	L	−163.80
40	300	500	L	−152.75
41	300	750	L	−152.78
43	300	1,000	L	−153.96
55	400	200	V	−13.04
116	400	200	V	−12.15
52	400	500	L	−138.50
51	400	750	L	−136.89
45	400	1,000	L	−135.42
		25.2 mole % propane		
75	200	200	L	−165.89
65	200	500	L	−166.64
62	200	750	L	−165.60
66	300	500	L	−144.98
67	300	750	L	−141.16
68	300	1,000	L	−142.22
76	400	200	V	−11.82
81	400	300	V	−24.82
80	400	400	V-L	−84.51
79	400	500	V-L	−112.81
78	400	630	L	−124.51
70	400	750	L	−127.38
69	400	1,000	L	−128.72
		49.8 mole % propane		
91	200	500	L	−156.72
83	200	750	L	−156.16
84	300	165	V	−11.58
85	300	300	V-L	−82.45
86	300	450	V-L	−109.20
88	300	585	L	−127.84
92	300	750	L	−132.06
90	300	1,000	L	−133.12
93	400	200	V	−9.98
94	400	500	V	−43.77
95	400	635	V-L	−62.27
96	400	775	V-L	−87.63
97	400	880	L	−98.11
99	400	1,000	L	−106.69
		79.7 mole % propane		
101	200	500	L	−138.65
100	200	750	L	−140.12
113	300	200	V	−15.54
107	300	500	V	−47.83
118	300	500	V	−50.97
105	300	600	V-L	−67.59
104	300	700	V-L	−85.87
103	300	820	L	−102.05
102	300	1,000	L	−113.07
109	400	200	V	−8.46
110	400	500	V	−23.93
117	400	500	V	−24.06
111	400	750	V	−37.01
112	400	1,000	V	−54.82
Run No.	Temp., °F.	Pressure, lb./sq. in. abs.	Phase	Δh, B.t.u./lb.

EXPERIMENTAL ERRORS

Errors which might be present in the experimental results due to heat leaks between the calorimeter and its surroundings or due to the flow of the fluid were checked by varying the flow rate while holding all other run variables constant. The flow rate was varied by changing capillary sizes and by the capillary partially clogging. Detailed data for the effect of flow rate on the experimental data is given by Yarborough (*31*). There was no apparent effect of flow rate on the experimental data.

Six replicates were run at 200°F. and 500 lb./sq. in. abs. for pure propane. The standard deviation for the six replicates was 0.59 B.t.u./lb. Six replicates are quite a small number to give a good estimate of the true standard deviation or absolute average error. However, the results should be somewhat indicative of the experimental error involved.

The limit of error for the experimental enthalpy differences was estimated by using a method of propagation of errors (*30*). The errors which were considered to enter into the equations used to calculate the experimental enthalpy difference were errors in (1) the measurement of the standard resistor electromotive forces, (2) the values of the standard resistors, (3) the stability of the power supply, (4) the measurement of the run time, and (5) the weight of the run sample. Measurements which do not enter into the direct calculation of the experimental enthalpy difference but which must be considered for corrections are (6) the temperature measurement and control, (7) pressure measurement and control, and (8) composition analysis. Another source of error could be due to the criteria set for accepting runs. Acceptable runs were those where the inlet and outlet temperatures varied not over 0.20°F. during the run and where the average inlet and outlet temperatures were within 0.50°F. of the desired run temperature. These criteria would allow a run to be accepted even though the system was not at true steady state. This error is very hard to determine, but the maximum error introduced by the acceptable run criteria was estimated to be about ± 0.2 B.t.u./lb. The estimated maximum experimental errors are given by Yarborough (*31*).

The observation of the data and the propagation of error calculations lead to an estimate that the maximum error possible in a run is on the order of 2 B.t.u./lb. The principal error is due to temperature measurement and control. The oil temperature bath evidently contained large temperature gradients (0.05° to 0.10°F.) which caused poor calibration results for the thermocouples and fairly unstable temperature control during a run.

The error due to the composition uncertainty is important for the mixtures. The propane-benzene binary was quite difficult to analyze because at room temperature and atmospheric pressure propane is a gas and benzene is a liquid. The method used to analyze by chromatography was to heat the sample bomb until the mixture was all in the gas phase and then inject the sample via a heated sample valve. A statistical analysis of the composition analyses showed a standard deviation of about 0.008 mole fraction and an absolute average error of about 0.006 mole fraction.

PURE COMPONENT COMPARISONS

The pure component propane enthalpy differences were compared with values from two enthalpy tabulations (*2*, *29*) and a Mollier chart (*9*). The absolute average differences between the experimental data and the values given by Edmister (*9*) was 0.71 B.t.u./lb., by Sage and Lacey (*29*) was 1.09 B.t.u./lb., and by API Research Project 44 (*2*) was 1.34 B.t.u./lb. The closest agreement between the experimental and literature values occurred at 400°F.

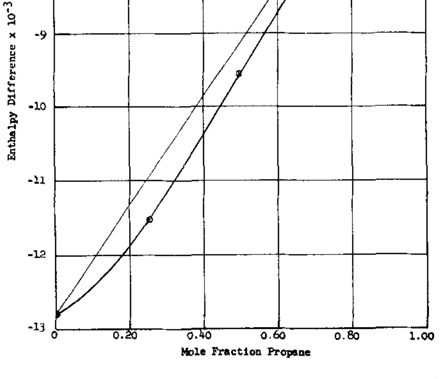

Fig. 3. Enthalpy difference as a function of composition at 200°F. and 750 lb./sq.in.abs.

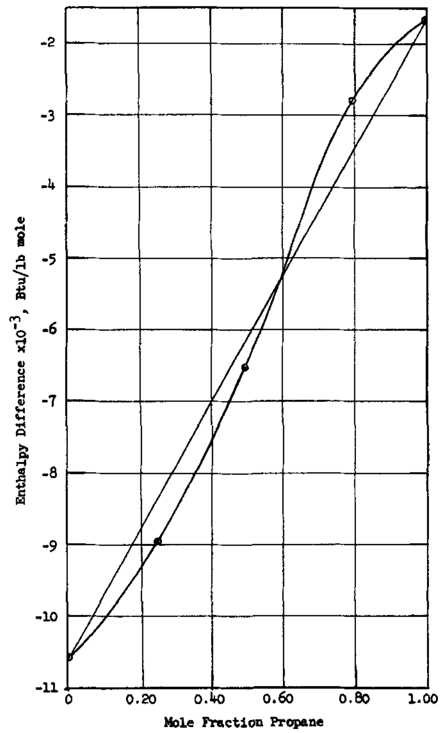

Fig. 4. Enthalpy difference as a function of composition at 400°F. and 1,000 lb./sq.in.abs.

The pure component benzene enthalpy differences were compared with values from two enthalpy tabulations (*21*, *23*). The saturated liquid enthalpy differences of Organick and Studhalter (*23*) agree quite well with the experimental data at 300° and 400°F. (0.05 and 0.60 B.t.u./lb., respectively) but differs by 4.6 B.t.u./lb. at 200°F. The enthalpy data of McCracken and Smith (*21*), which were measured on an isobaric calorimeter, do not agree very well with the benzene enthalpy differences obtained in this work. The absolute average difference between the benzene enthalpy data of McCracken and Smith and the enthalpy data obtained in this work is 4.6 B.t.u./lb.

A third set of benzene enthalpy differences were available in the literature. These data were obtained by Gilliland and Lukes (*11*) using a calorimeter similar to the one used in this work. However, the authors are sure that the results of Gilliland and Lukes were affected by a heat leak (*31*). The data of Gilliland and Lukes are scattered but generally agree fairly well with the data of McCracken and Smith (*21*). To these authors' knowledge, the Purdue calorimeter (*21*) has never been used to obtain enthalpy data for comparison purposes with other enthalpy data in the literature. In view of the results for propane and benzene just mentioned, such a comparison would appear to be desirable.

ENTHALPY CALCULATION METHODS

Three equations of state were used to calculate vapor phase enthalpy differences for the propane-benzene system. These equations were the Redlich-Kwong (*28*), the Benedict-Webb-Rubin (BWR) (*3*), and the virial equations of state.

The Redlich-Kwong equation of state was used because it is a simple, generalized equation which has been reported to fit experimental data better than any other two-constant equation of state (*28*). The equations used to calculate the enthalpy difference via the Redlich-Kwong equation of state have been given (*10*). Enthalpy differences calculated via the Redlich-Kwong equation are compared with the experimental data elsewhere (*31*).

The comparisons are not good except for pure propane at 300° and 400°F. However, this could have been expected for two reasons: the Redlich-Kwong equation was recommended for use only above the critical temperature of the fluid, and no component heavier than butane was considered when the equation was formulated.

The BWR equation of state was used because it has eight specific constants which can be adjusted to fit experimental data quite accurately. This equation has been used extensively to calculate thermodynamic properties of pure components and mixtures. Enthalpy differences calculated via the BWR equation are compared with the experimental data elsewhere (*31*). The propane and benzene constants for the equation were obtained from the literature (*3, 23*).

The comparisons are quite good for pure propane and are fairly good for the superheated mixture data. The one benzene comparison is not good. The saturated vapor enthalpy differences predicted by the BWR equation did not compare at all well with the experimental data. Part of the discrepancy in the comparison of the superheated vapor enthalpy differences is undoubtedly due to the benzene constants used.

The virial equation of state was used because it is based on theory (*14*). Second and third virial coefficients were available for both propane (*8, 22*) and benzene (*1, 5, 7, 8, 19*) for the temperature range of interest. Also second virial coefficients were calculated from the equation presented by Pitzer and co-workers (*20*), and third virial coefficients were calculated by the general method of Prausnitz (*25*). The methods used to calculate the interaction second virial coefficients were the Kihara potential (*17, 18*) which has been used to predict second virial coefficients very well for both propane (*5, 27*) and benzene (*5*), the empirical method of Prausnitz (*25*) which is based on the corresponding states equation of Pitzer and co-workers (*20*), and the empirical method of Huff and Reed (*15*) which is based on the corresponding states of Pitzer and co-workers (*20*). The methods used to calculate the interaction third virial coefficients were the empirical method of Prausnitz (*25*) which is a corresponding states type of correlation and the empirical method of Connolly (*6*).

The comparisons between enthalpy differences calculated via the virial equation and experimental data (*31*) show that the enthalpy differences based only on second virial coefficients fit the data quite well up to 500 lb./sq. in. abs. Above this pressure the second virial coefficient calculation method would give too large an enthalpy difference, and then finally the calculated volume would become imaginary. This feature caused the second virial coefficient calculations to agree fairly well with the experimental saturated vapor enthalpy differences. The comparisons (*31*) also show that the enthalpy differences based on the second and third virial coefficients fit the superheated vapor data quite well up to 1,000 lb./sq. in. abs.

The principle of corresponding states was used to calculate enthalpy differences for the same conditions the experimental data were taken. The generalized modified corresponding states correlation of Pitzer and co-workers (*20*) was used for both the pure components and the mixtures. The application of the correlation for calculating enthalpy differences for the pure components is straight forward, but the application of the correlation to mixtures is not.

The pseudocritical concept proposed by Kay (*16*) was used with the generalized correlation to calculate enthalpy differences for the mixtures. Two papers concerning modifications (*24, 26*) of Kay's pseudocritical rule have been published recently, and both showed that Kay's rule applied quite well to the propane-benzene binary system. The small correction recommended by Pitzer and Hultgren (*24*) was employed when calculating the pseudo acentric factor for the mixture. The generalized method of Prausnitz and Gunn (*26*) for calculating pseudocritical variables has been shown to be satisfactory in previous work (*4*).

The comparisons between the calculated and experimental enthalpy differences (*31*) are quite good. In most cases the vapor phase enthalpy differences calculated with the corresponding states correlation agree as well as those calculated by the equations of state. The calculated saturated vapor enthalpy differences for the mixtures do not agree very well with the experimental data. The agreement of the calculated liquid phase enthalpy differences with the experimental values was very good except when the critical conditions were approached.

CONCLUSIONS

Experimental apparatus was designed, constructed, and operated which could be used to measure the isothermal pressure effect on the enthalpy of liquids and vapors. The isothermal integral heat of vaporization of a mixture could be obtained directly from the data, and the isobaric integral heat of vaporization could be obtained if enough data were taken. The apparatus was used to obtain data on pure components and mixtures. The estimated maximum error of the experimental data is 2 B.t.u./lb.

The virial equation of state appears to be adequate for gas and superheated vapor enthalpy difference calculations for pure components and mixtures when one of the methods listed in this paper is used to obtain virial coefficients. The second virial coefficient could be relied upon to about 500 lb./sq. in. abs., and both the second and third virial coefficients gave good results to 1,000 lb./sq. in. abs. The Benedict-Webb-Rubin equation of state agreed quite well with the experimental data for propane and fairly well with the mixture data. The benzene constants evidently were not very good. The Redlich-Kwong equation of state should not be applied to the propane-benzene system at the conditions used in this work. None of the equations of state predicted the saturated vapor enthalpy differences satisfactorily.

The corresponding states correlation of Pitzer and co-workers used for predicting liquid and vapor enthalpy differences for the pure components and mixtures agreed quite well with the experimental data. The only data that were not predicted very well were the saturated vapor enthalpy differences and enthalpy differences near the critical point. The modification of Kay's pseudocritical rule by the method of Pitzer and Hultgren or Prausnitz and Gunn is recommended for mixtures when the correlation is used.

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A Study of Perfectly Mixed Photochemical Reactors

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The performance of a perfectly mixed photochemical reactor has been analyzed for systems having low light absorption coefficients. The analysis has been tested by an experimental study of the decomposition of hexachloroplatinic acid in dilute aqueous solution. Results tend to verify the analysis, but indicate the need for additional experimental work.

Although photochemistry continues to develop as an important branch of theoretical chemistry, industrial applications of photochemical processes have been notably few. Since photochemical reactions sometimes offer distinct advantages over thermal reactions, this situation is perhaps surprising. One of the contributing factors may be the lack of quantitative procedures for the design and scale-up of suitable reactors. This is a complex problem, more difficult than the usual chemical reactor problem, which represents a challenging area for chemical engineering research and development. Unfortunately, the problems of design and analysis of photochemical reactors have received only sporadic attention in the chemical engineering literature during the last fifteen to twenty years. In view of this situation, it was decided to initiate a research program into photochemical reactor design and scale-up. The present paper presents the results of one such investigation into the behavior of perfectly mixed reactors.

PREVIOUS WORK

Previously reported studies of photochemical reactor design have all dealt essentially with continuous flow reactors of the tubular type. The first investigation in recent years was reported by Baginski in 1951 (*1*). He studied the reaction of hydrogen sulfide and n-1 octene in the liquid phase, using a tubular reactor irradiated from the

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