

SPECIFIC HEATS OF SOME HYDROCARBON SOLUTIONS

Thesis by
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In Partial Fulfillment
of the
Requirements for the Degree of
Master of Science

California Institute of Technology
Pasadena, California

1935

Introduction

Hydrocarbons as they occur in nature are in general very complex mixtures. If one wishes to discover the basic relations governing their physical behavior, it is obviously best to study first the simple and work through to the complex. However, even a study of all the individual chemical components in natural hydrocarbon mixtures would be inadequate, if one's aim is to use the results of such studies in aiding the petroleum industry. Knowledge of the behavior of mixtures is desired. Consequently, in the American Petroleum Institute Project No. 37, those mixtures have been studied which would yield results capable of immediate application and also useful in more fundamental investigations of hydrocarbon behavior.

The type of work which is reported here represents one phase of those studies. The specific heat data are only a part of those required to make up a complete picture of the thermodynamic behavior of given mixtures. However, specific heat values for substances, apart from any other thermodynamic considerations, are of direct value. Consequently, an examination of them may be of interest. It is the purpose of this thesis to set forth the experimental methods and results of studies on a few comparatively simple mixtures. Only the specific heat of the liquid phase is determined by the method here discussed.

In the work of Project No. 37, emphasis is placed on studies of mixtures of oil and gas under various conditions

of pressure and temperature. The pressures go as high as 3000 pounds per square inch. In a specific heat calorimeter, then, the bomb to hold the sample must be able to withstand this pressure.

Earlier work had been done using a calorimeter now discarded. It consisted of a steel bomb on a heat-insulating mounting which could be rotated (for agitating the contents)-- all contained in a double-walled jacket, having circulating oil in the walls which was kept automatically at the same temperature as that of the surface of the bomb. After considerable work on developing the technique of operation of this apparatus, the error in results was reduced to, at best, 1.5 % and generally about 5 to 8 %. The main source of inaccuracy lay in the fact that the heat capacity of the bomb was about five times that of the contents. Thus, the specific heat capacity of the contents was calculated from the difference of two large quantities. Also the oscillation of the bomb to agitate the contents caused forced convection of the air in the jacket, and any slight inequality of temperature of jacket and bomb caused an appreciable heat transfer.

On the basis of experience obtained in the operation of this first calorimeter, a new one was designed and built. The essential changes made were to make a new bomb of high strength and low heat capacity, and to enclose this bomb in a highly evacuated chamber. Also a different type of insulating mounting for the bomb was used. The former mounting consisted essentially of a micarta collar holding the bomb, supported by trunnions going through the walls of the jacket.

The steel backing for the micarta had considerable heat capacity, and the surface of micarta in contact with the bomb was excessive. As a result, there was a slow flow of heat which made the time to reach constant temperature so long that other errors became appreciable. The new bomb is supported in wire-wheel fashion by three pairs of fine piano wires in a light steel ring which is carried on the trunnions. It is designed for working pressures up to about 600 pounds per square inch, and its heat capacity is about one fifth to one half that of the contents. Since its working pressure limit is only 600 pounds, the range of substances and mixtures studied was correspondingly limited. In view of the success in the use of special steel alloys in the construction of the new light bomb, it seems feasible to build one to withstand 3000 pounds per square inch, and thus to extend the range of study.

With the present instrument an accuracy of 1 to 1.5% is obtained for the specific heats of most systems. A considerable number of systems have been studied, but, for reasons given below, only two are reported here.

Mixtures Chosen for Study

Two series of mixtures have been chosen as subjects for this report. The first is a series of liquid mixtures of propane and crystal oil, the latter being a heavy, highly-refined, stable hydrocarbon oil. The second series consists of liquid mixtures of n-butane and crystal oil. These two were chosen for two reasons. First, the pressure

range for these systems is suitable for the light bomb. Second, there have been determined previously in this laboratory all the necessary supplementary isothermal data for converting the observed values of specific heat at constant volume to specific heat at constant pressure.

Materials

The propane used was obtained from the Philgas Company. They made a special analysis of this lot of propane and reported:

Ethane	None
Propane	100%
Isobutane	None

The normal butane was obtained from the same source. A special analysis of it showed:

Isobutane	0.18%
N-butane	99.21
Isopentane	0.61

The crystal oil is a highly refined water-white oil. It was chosen for this and other studies because it fulfilled the desired conditions of a liquid of rather high viscosity with a narrow range of boiling point and composition. It is stable with respect to time and temperature, that is, measurements of its properties are reproducible in spite of heating within the experimental range and in spite of long standing. Also, its vapor pressure is not appreciable within the range studied. Some of its properties are as follows:

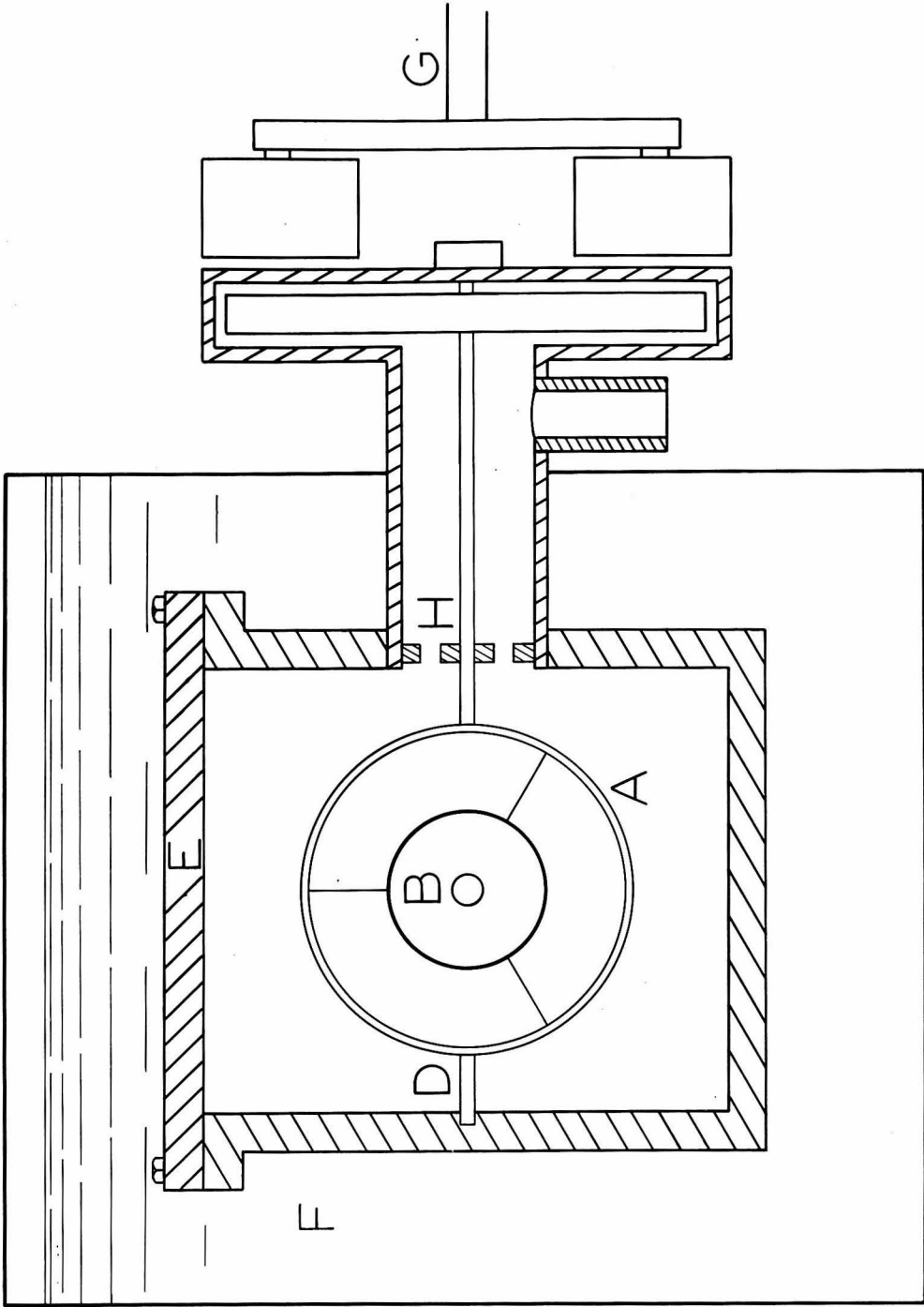


FIGURE I

Sp. gr. (100°/39.2° F)	0.8665
Gravity °A.P.I. (60°F)	29.1
Viscosity at 200° F	40.5 millipoises
Aver. Molecular weight	337.5

Method and Apparatus

The general method of measurement is conventional. A weighed sample of the substance to be studied is placed in a bomb. The bomb is shaken until its temperature is uniform. A known amount of heat is added electrically, and the corresponding rise in temperature is observed. From these data a value of the specific heat at constant volume may be calculated.

In figure 1 is shown a diagrammatic cross section of the calorimeter. The bomb (B) is supported by three fine steel piano wires fastened to the ring (A). This ring is carried on trunnion bearings (D, H), allowing the whole bomb assembly to be oscillated through about 90°. The space surrounding the bomb, within the jacket (E) is pumped down to a vacuum of 10^{-5} to 10^{-3} mm of mercury. The oscillation of the bomb is effected by means of the extended shaft (H). On the end of this shaft is fastened a steel bar or armature. It is free to rotate with the shaft within the flat cylindrical chamber shown. This latter chamber is evacuated also. Outside of this chamber is mounted an oscillating electromagnet (G). With the aid of the magnetic coupling between the magnet and the steel armature, one is enable to get mechanical agitation in the

bomb, without any direct coupling through packing glands which would make difficult the attainment of high vacuum. The interior of the jacket is chromium plated, and the surface of the bomb is nickel plated in order to minimize radiation heat transfer due to momentary differences in temperature. By maintaining the vacuum at or below 10^{-3} mm of mercury, heat transfer by conduction and convection is reduced to the position of a minor factor. The whole jacket (F) is surrounded by circulating oil kept automatically at the proper temperature. The oil bath consists of a double walled can in which baffles are provided so as to give a symmetrical flow of oil over the whole outer surface of the jacket (F). The electric heater for this oil is located within the circulating pump, so that no local "hot spots" occur in the bath. The temperature of this bath is so regulated that the inner surface of the jacket (F) is at all times during the run within about 0.02°F of the surface of the bomb. When this condition existed, the conventional calorimeter curves were not drawn, for it was found that the temperature of the bomb would neither rise nor fall by more than 0.02°F in an hour. This automatic control of surface temperatures depended upon a thermocouple device. One thermocouple junction was placed on the outer surface of the jacket (F), and the other in series with it was placed on the outer surface of the bomb. The two leads from this couple ^{went} to a high-sensitivity galvanometer, the light-beam of which actuated a photo-electric cell. It was this cell which, through relays, controlled the heaters

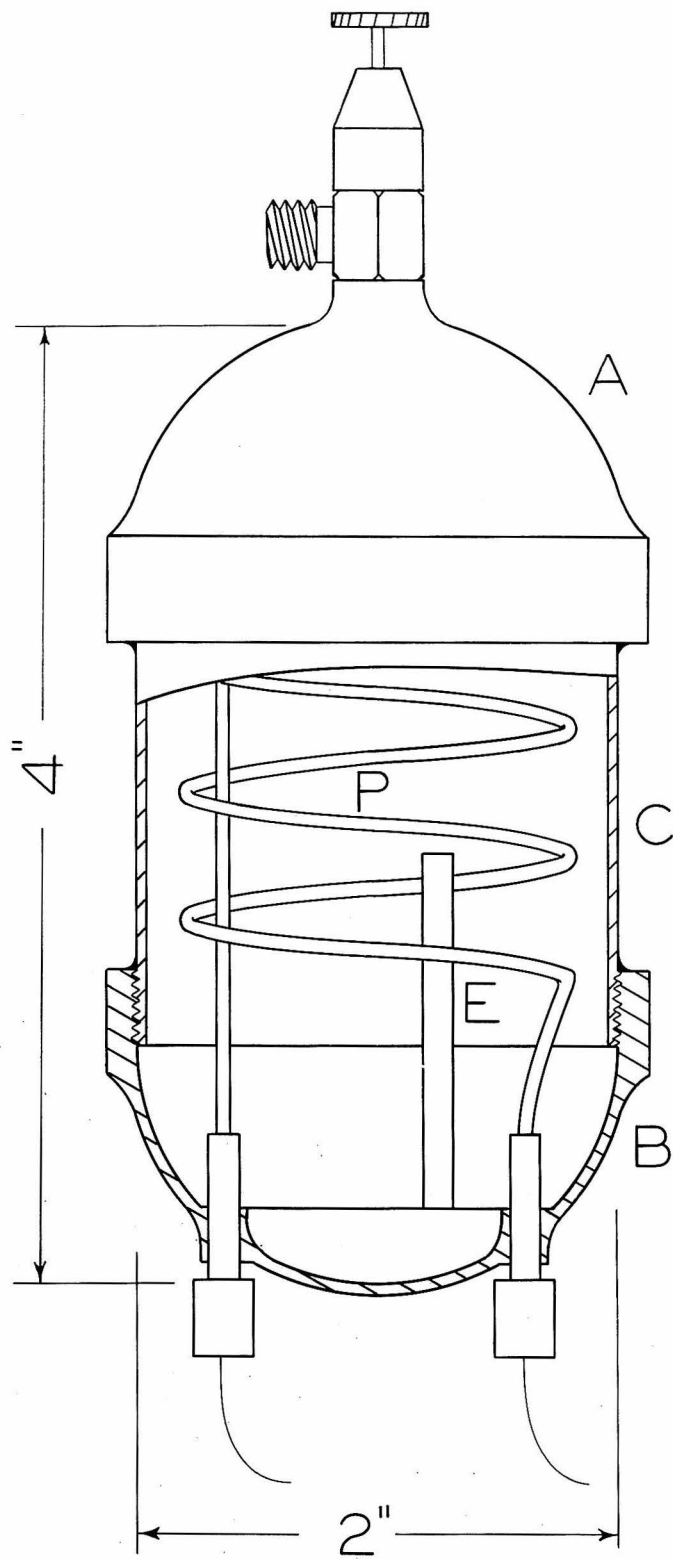


FIGURE 2

in the oil bath. Thus, whenever the temperature of the bomb was rising during the measured energy input, the thermocouple control would cause the oil bath to heat at exactly the same rate as the bomb. When the energy input ceased, the bath temperature would become constant as soon as did that of the bomb.

As a final aid in maintaining temperature stability, the whole calorimeter was set in an air thermostat which was kept within 3° of the bomb temperature. This gave the control system a chance to regulate over a much narrower variation range.

A detail diagram of the bomb is shown in Figure 2. The two bell ends (A, B) and the cylindrical body (C) were ground from bar stock of a special high tensile strength steel alloy (90,000 lbs/ sq. in. tensile strength). When finally ready for assembly, the threads of the three parts were tinned, and during assembly, the whole was sweated together. In order to avoid leaks, no electrical leads were bushed through the walls of the bomb. The electric heater for giving the measured energy input to the bomb was enclosed in a spiral of stainless steel tubing (P), and this went through the wall at a soldered joint. The thermocouple for the accurate measurement of the temperature of bomb and contents was encased in the deep well (E), which extended into the bomb about a third of its length. The samples of oil and gas were introduced through the connection and diaphragm valve shown at the top. The whole bomb assembly weighed about 250 grams, having a volume of

about 160 cc. The mass of sample was obtained by weighing the bomb before and after filling. Because of the lightness of the bomb, errors in this operation were inappreciable.

As mentioned above, the temperature of the bomb was measured by thermocouple. This was a copper-constantin couple, and, to eliminate stray e.m.f.'s, the constantin wire was all one piece from hot to cold junction. The cold junction was in an agitated ice bath. The couple was calibrated by immersing a calibrated mercury thermometer in the surrounding oil bath, and measuring the thermocouple e.m.f. after the system had been steady for a considerable time. This method assumed that the bomb and bath were at the same temperature, and this assumption seemed to be born out by observation. At any rate, any given point on the calibration curve should be accurate to about 0.04°F , and a smooth curve drawn through all the points should allow one to calculate temperature rises somewhat more accurately. The usual temperature rise was about 10°F , and so the error in this measurement may be about 0.2%. The potentiometer used in this work was similar to the Wolfe type instrument, and it had been calibrated against a Bureau of Standards instrument. One could measure temperature variations easily down to 0.005°F with the cold junction at 32°F .

The energy input to the bomb was determined by measuring power input and time of input. The time of input was standardized at 20 minutes and was measured by a counter

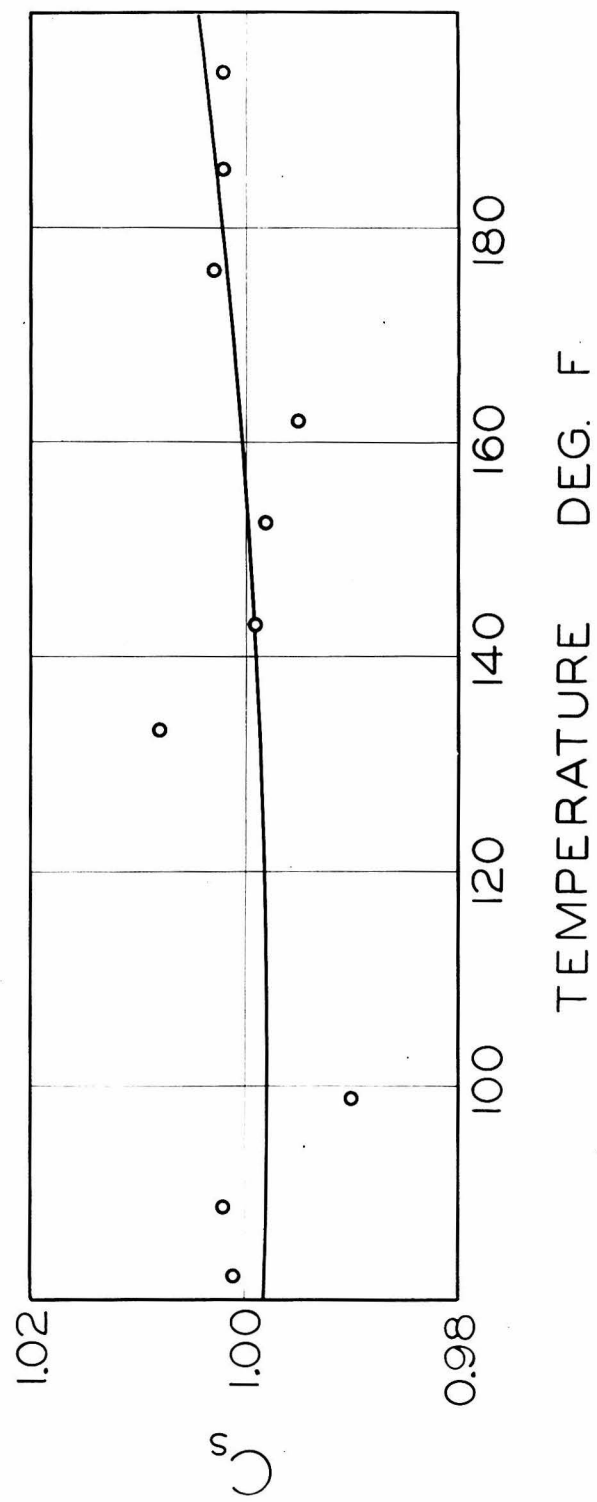


FIGURE 3

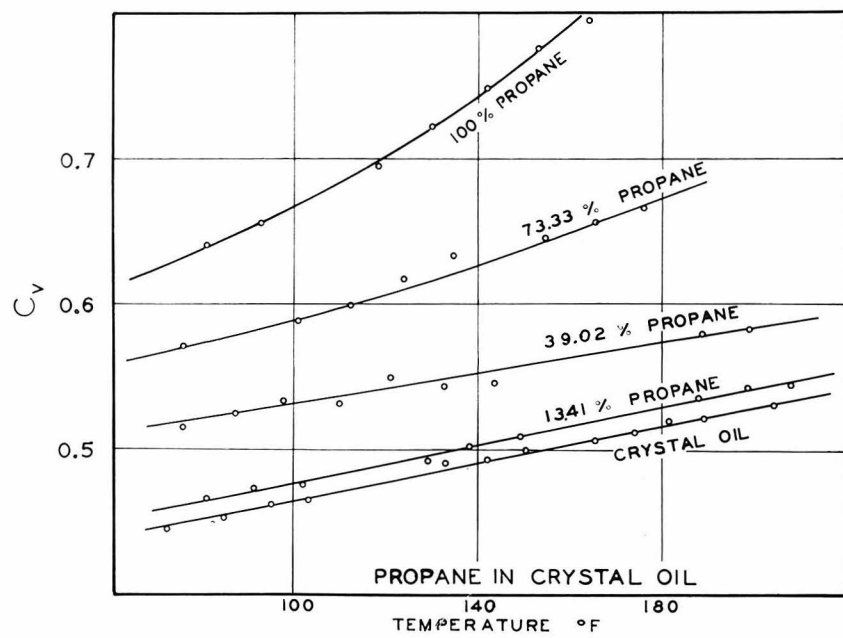
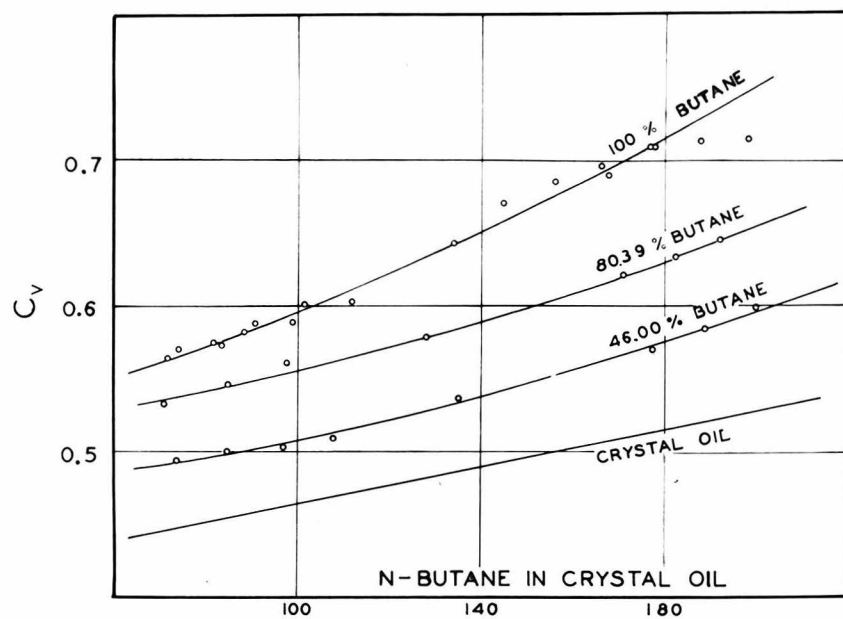
run by a synchronous clock motor. The wattage was determined several times during a run by measuring the direct current voltage at the terminals of the bomb and the current flowing. A device was arranged so that the watts input was essentially constant during the 20 minutes, and so no integration was necessary to arrive at a total energy value. These voltage and current values were determined by the use of a Leeds and Northrop Student Potentiometer and were probably accurate to about 0.1%.

The heat capacity calibration of the bomb itself was carried out with the bomb filled with hydrogen at one atmosphere. Here some difficulty was experienced in attaining equilibrium between the main mass of the bomb and the thermocouple. After several tries, a satisfactory calibration curve was obtained. To check it, however, a run was made on the specific heat of water. The results of this run are shown in Figure 3. The calibration that was finally used in subsequent calculations may be in error by as much as 3%. The resultant effect on the specific heat calculated for the contents, was an error of 1.5 to 0.6%.

Thus, the factor which contributes most to the experimental errors is the uncertainty in the heat capacity of the bomb. This error would make all the values wrong by some absolute amount. If there were no other appreciable errors, the experimental data would still lie on smooth curves. Since they do not, it is evident that there must be other contributing factors. They probably arise from the technique of operation. After the bomb has been

standing at equilibrium for half an hour, with the photoelectric control working perfectly, one suddenly turned on the heat to the bomb. The sudden flow of heat to the surface caused the control to hunt, and because of the natural lag in flow of oil to the control junction, the hunting was sometimes disastrous. The same trouble arose when the heat input was cut off. Various methods of operation were tried to overcome this difficulty, and by care it could largely be eliminated. However, it is nearly certain that this was the chief cause of scattering error in the earlier runs.

One other effect which should be noted concerns the nature of the contents of the bomb. For very fluid substances such as liquid propane, after a given heat input had been completed, the bomb and contents reached their final equilibrium temperature very quickly, say within six minutes. On the other hand, for viscous substances, like the crystal oil used here, the temperature would approach its final value in a slow, asymptotic manner, sometimes taking as long as forty minutes to reach a satisfactory steady state. Since the viscosity of these mixtures decreased considerably with temperature, one might expect greater consistency of values at the higher temperatures. Experimentally this was found generally to be the case. As a matter of standard technique, however, the bomb was allowed to stand for about forty minutes after the twenty minutes heating. This gave more complete assurance of the attainment of equilibrium.



DIRECT EXPERIMENTAL DATA
 SPECIFIC HEAT AT CONSTANT VOLUME

FIGURE 4

Results

The specific heat as calculated directly from the above measurements is a specific heat at constant volume. However, it is not C_v for the liquid in the bomb. In a bomb of this type there must always be some gas space, and consequently two phases in equilibrium. Thus, whenever the bomb is heated, some of the more volatile component will pass out of the liquid phase, and the heat absorbed in this vaporization will appear to increase the specific heat of the contents. The larger the gas space present, the greater will be the magnitude of this effect. Thus, for every different sample, C_v as measured will be different. For this reason, no direct experimental data have been tabulated. An idea of the accuracy of the measurements may be gained from an examination of Figure 4. From the smoothed curves shown, values have been taken and converted to specific heats for the liquid in the condensed region, at a pressure only infinitesimally greater than that at which the first trace of gas is liberated from the liquid phase (the bubble point).

It is the purpose of this section to indicate the operations by which these conversions were made. All the data for them were obtained from pressure-volume-temperature data for the substance in question.

First let us consider the case of a pure compound, such as butane, since its treatment is somewhat different from that of a mixture. For the heat absorbed by vaporization, the following correction is made ⁽¹⁾ :

$$C'_V = C_V - \frac{L_2 x_2 - L_1 x_1}{\Delta T} + \left(\frac{Lx}{T} \right)_{\text{mean}} \quad (\text{I})$$

C'_V is C_V in the two phase region but corrected for vaporization

L is the latent heat of vaporization

x is the quality or fraction of mass in the gas phase

ΔT is the rise in temperature of the run in question

1 and 2 refer to values at T_1 and T_2 , the initial and final temperatures for the run

L may be calculated from vapor pressure data and the Clapeyron equation. x , the quality, may be evaluated from a consideration of the specific volumes of the two phases and the specific volume of the system in the bomb. For this it may shown from a simple balance of masses and volumes that

$$x = \frac{v_b - v_l}{v_g - v_l} \quad (\text{II})$$

v_b is the sp. vol. of the system in the bomb

v_l is the sp. vol. of the liquid

v_g is the sp. vol. of the vapor

All these and the following corrections are best made by calculating a few correction terms and plotting them against temperature and using the curve for correcting all values across the temperature range for that particular substance.

Next the heat capacity of the gas phase must be considered. When vaporization has been accounted for, we may write for the specific heat of the two phase system

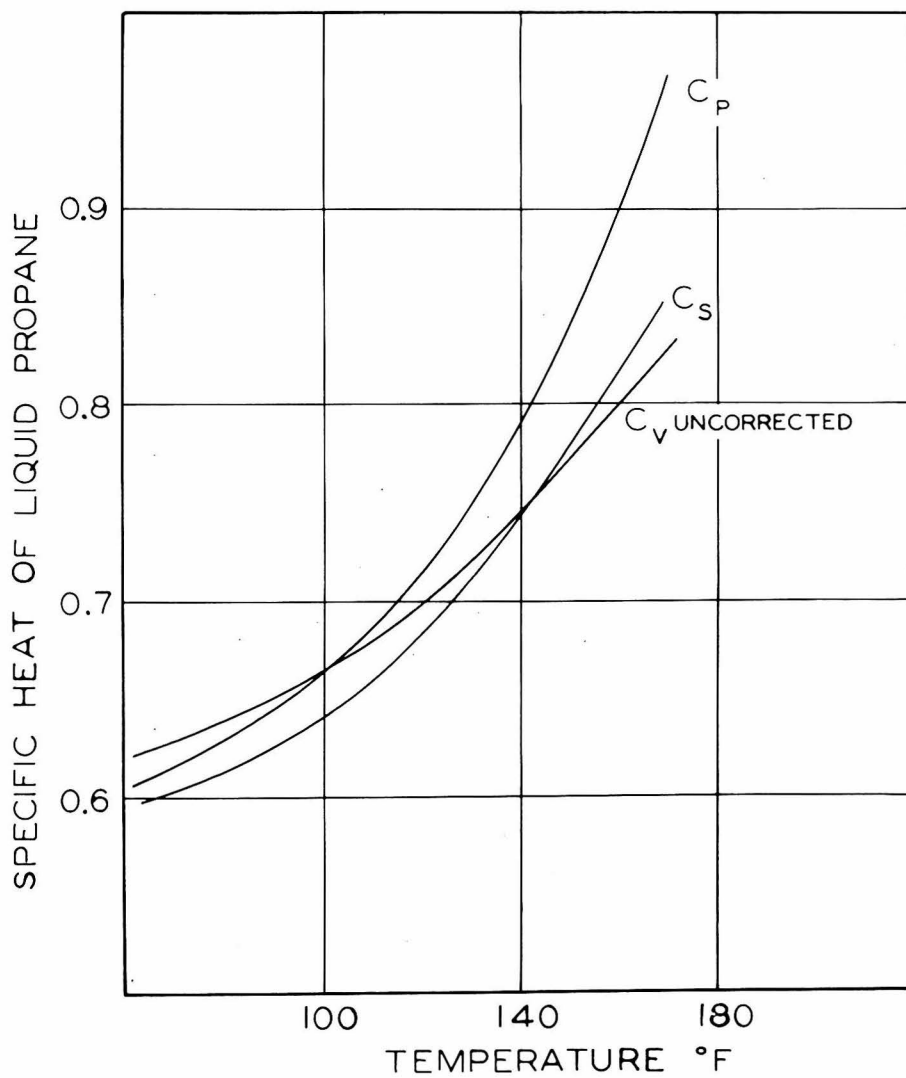


FIGURE 5

$$C = C_g x + C_l (1-x)$$

$$C_l = \frac{C - C_g x}{1-x} \quad (\text{III})$$

where x is quality.

When the bomb is nearly full, x is very low, and the correction is almost negligible. A very rough guess at the value for C_g , the specific heat of the gas, will suffice.

When this correction has been applied, we have the specific heat of the liquid under saturation, usually written C_s . This quantity is described simply as $(1/w)(dq/dT)$ under bubble point conditions when in infinitesimal but constant amount of gas phase is present. To convert from this to C_p for the liquid just above bubble point pressure, we will use the relation ⁽²⁾

$$C_p = C_s + \left(\frac{\partial v}{\partial T} \right)_p \cdot \frac{L}{v_g - v_l} \quad (\text{IV})$$

where L is the latent heat of vaporization

v_g is the sp. vol. of the vapor

v_l is the sp. vol. of the liquid.

The partial derivative is the thermal expansion of the liquid as constant pressure, and may be evaluated by taking slopes on the curve of saturation volume vs T for the saturated liquid. This conversion term is of quite appreciable magnitude, and care is necessary in evaluating it.

An idea of the size of these corrections may be gained from Figure 5. In it are shown for the case of propane:

(1) C_v , specific heat at constant volume as experimentally

determined, before any correction terms have been applied. It is to be noted that this is not the C_v for the liquid at the bubble point. (2) C_s , the specific heat of the liquid at the bubble point as defined above. (3) C_p , the specific heat at constant pressure for the condensed liquid at a pressure just above bubble point pressure. The fact that the C_v and C_s curves cross each other is unusual, but is readily explained. Ordinarily, by reason of vaporization, the apparent specific heat C_v is greater than the specific heat under saturation conditions, C_s . However, with propane, in the upper temperature range, the liquid is expanding so fast with rise in temperature that the vapor space is actually decreasing. A calculation of the quality x by the equation (II) given above for it, would show that the quality was decreasing with temperature rise in this range. This means that with this rise, some propane is condensed. Heat evolution attends this process, and so the apparent specific heat C_v is lower than C_s , meaning that the curves must cross somewhere in the higher temperature range.

The reason for the increasing correction for C_p may be seen from Equation (IV) used above, written in a different form:

$$C_p = C_s + T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_{\text{sat}} \quad (V)$$

As the critical point of propane is approached, the derivative $(\partial v / \partial T)_p$ for the liquid is approaching infinity, and so $(C_p - C_s)$ is likewise approaching infinity.

At first glance, also, it may seem strange that C_v is greater than C_p in the lower temperature range. It is not correct, however, to make this comparison. The C_v shown, it will be remembered, is the experimental value for the system in a different state than that for which C_p is shown. From an inspection of Equation (VIII) given below, it may be seen that C_v , the specific heat of the liquid on the single phase side of the bubble point, is a curve lying continuously below C_g by an amount equal to $T(\partial p/\partial T)_v (dv/dT)_{\text{satn}}$, where the $(\partial p/\partial T)_v$ is for the liquid on the single phase side of the bubble point. This term for condensed liquids at constant volume is, of course, quite large as compared with the same derivative in the two phase region, and the correction would probably throw the C_v curve considerably below the C_g curve. At all events, the three curves (C_p , C_g and C_v) for the single phase system at bubble point would lie one above the other with no crossing over.

For mixtures, the calculation is slightly different. To take care of the two phase corrections, we may use the convenient equation:

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad (\text{VI}) \quad (4)$$

By its use we may convert the observed C_v to the C_v when only an infinitesimal amount of gas phase is present. For most of the mixtures studied, the volume of gas space in the bomb was comparatively small, and the fraction of the

gaseous component which was in the gas phase was also small. Consequently, the composition of the liquid phase differs only very slightly from that of the system as a whole. A consequence of this is that the pressure existing in the bomb was only slightly less than the bubble point pressure for that mixture. Now, since the pressure remains essentially constant as the volume is changed, their derivatives against temperature will also be constant. Also $(\partial^2 p / \partial T^2)_v$ will be closely equal to $(d^2 p / dT^2)_{\text{satn}}$. From a plot of bubble point pressures against temperature, for the given mixture, one obtains the first derivative $(dp/dT)_{\text{satn}}$ and from a plot of this against temperature, one obtains the desired second derivative. Now, since this derivative does not change appreciably with volume, we may write the equation as

$$\Delta C_v = T \left(\frac{d^2 p}{dT^2} \right)_{\text{satn}} \Delta v.$$

Since the volume is being decreased from bomb volume to bubble point volume, C_v for the liquid just on the two phase side of the bubble point will be smaller than the observed C_v .

Having obtained C_v for the liquid just on the two phase side of the bubble point, we may use two thermodynamic relations to convert to C_p for the liquid just on the one phase side.

$$C_s = C_p - T \left(\frac{\partial v}{\partial T} \right)_p \cdot \left(\frac{dp}{dT} \right)_{\text{satn}} \quad (\text{VII})$$

$$C_s = C_v + T \left(\frac{\partial p}{\partial T} \right)_v \cdot \left(\frac{dv}{dT} \right)_{\text{satn}} \quad (\text{VIII})$$

Since we are now dealing with the system still in two phases, with only a minute amount of gas phase, it is quite closely true that

$$\left(\frac{\partial p}{\partial T}\right)_p = \left(\frac{dv}{dT}\right)_{\text{satn}}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{dp}{dT}\right)_{\text{satn}}$$

With these equalities holding, we may eliminate C_s and write

$$C_p = C_v + 2T \left(\frac{dv}{dT}\right)_{\text{satn}} \cdot \left(\frac{dp}{dT}\right)_{\text{satn}} \quad (1X)$$

The volume derivatives may be obtained from slopes on a plot of bubble point liquid volumes vs temperature for the mixture. The pressure derivative is likewise obtained from a bubble point pressure vs temperature plot

One must be watchful in the use of equations such as these to make a clear distinction between properties on the one phase side and one the two phase side of the bubble point. Most of the properties, such as C_p and C_v and these derivatives, undergo discontinuities as the boundary is crossed. However, C_s is a property which has significance only on the boundary, but the concept is still valid at infinitesimal distances on either side of the boundary. It is for this reason that specific heats were converted from C_v for the two phase system through C_s to

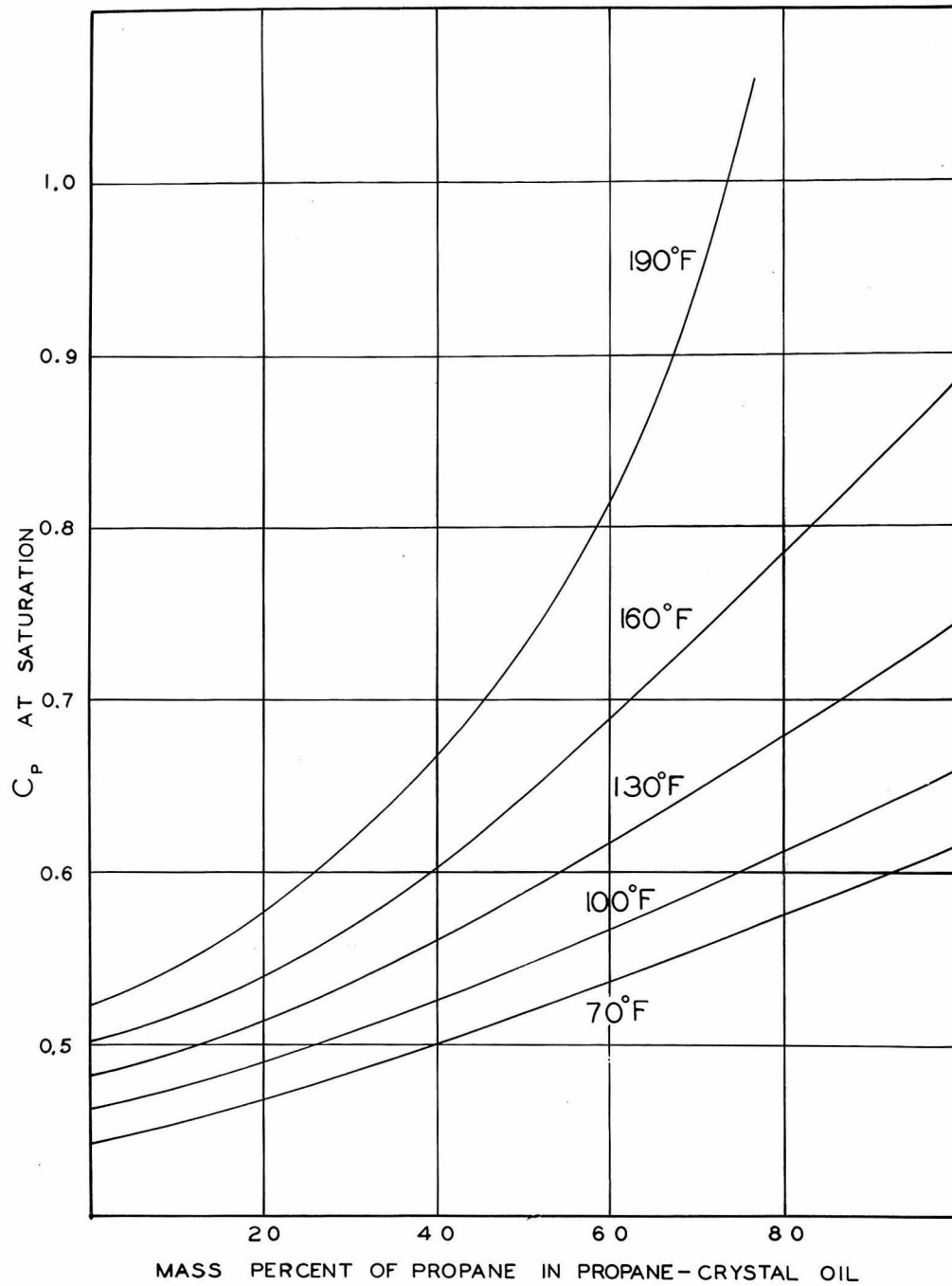


FIGURE 6

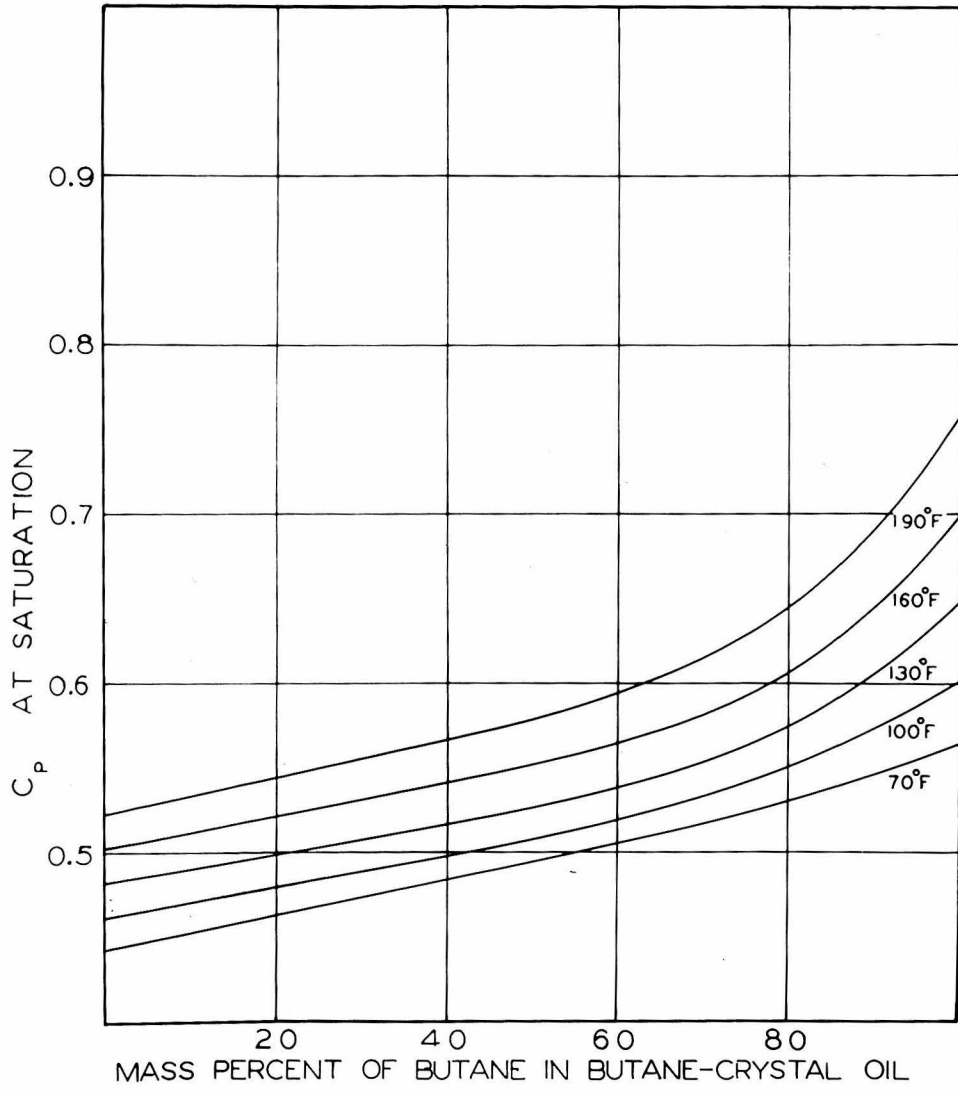


FIGURE 7

C_D for the liquid on the one phase side of the boundary.

A numerical example, carrying these calculations out for one specific case, is given in an appendix.

In Figures 6 and 7 are shown the results of the studies on the systems propane-crystal oil and n-butane-crystal oil respectively. The experimental points are not shown, since all the points lay on the smooth-drawn curves shown for the butane system, and likewise for the propane system with one exception. The mixture containing 13.41% propane was systematically low by 1 to 3%. This seems almost evident from a rough inspection of the plot of the original data (figure 4). However, in spite of this one poor set of data, the remaining material is complete enough so that a very satisfactory curve against composition may be drawn. In Tables 1 and 2 are recorded values taken from these smooth curves. The value for pure propane at 190°F is not shown because experimental data did not extend to this temperature, nor near enough to it to make an extrapolation warranted.

The final overall maximum error in these figures is estimated to be 1.5%.

Table 1 Propane-Crystal oil System

SPECIFIC HEAT AT CONSTANT PRESSURE
FOR THE BUBBLE POINT LIQUID

Temp °F	Mass percent of Propane in the mixture					
	0%	20%	40%	60%	80%	100%
70	0.442	0.467	0.500	0.536	0.575	0.617
100	0.462	0.489	0.526	0.567	0.612	0.661
130	0.482	0.512	0.560	0.617	0.679	0.746
160	0.502	0.538	0.602	0.689	0.785	0.886
190	0.523	0.576	0.667	0.815	--	--

Table 2 N-butane--Crystal Oil System

SPECIFIC HEAT AT CONSTANT PRESSURE
FOR THE BUBBLE POINT LIQUID

Temp °F	Mass percent of Butane in the mixture					
	0%	20%	40%	60%	80%	100%
70	0.442	0.461	0.483	0.505	0.530	0.564
100	0.462	0.479	0.498	0.519	0.550	0.601
130	0.482	0.498	0.517	0.538	0.574	0.647
160	0.502	0.521	0.541	0.564	0.605	0.699
190	0.523	0.545	0.567	0.595	0.645	0.758

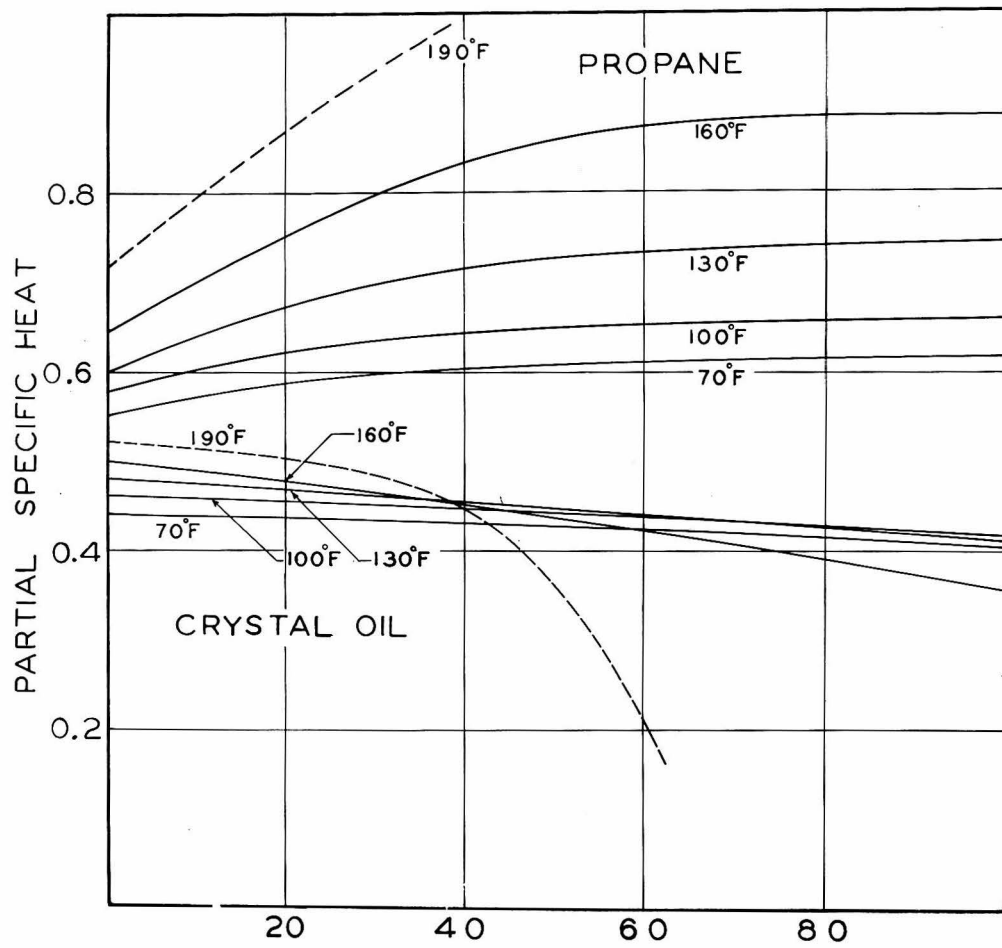
Discussion

It is evident from Figures 6 and 7 that the specific heats of the components cannot be considered as additive. If they were, these curves would be straight lines across the whole range of composition. At the lower temperatures they seem to approach this condition, but the departure is rapid for any appreciable rise above 70°T. They are, nevertheless, regular in their behavior. To investigate the possibilities of this regularity, recourse is made to a quantity called the partial specific heat capacity,⁽⁴⁾

This heat capacity is a property of a component in a mixture which plays a role thermodynamically identical with the corresponding heat capacity of the same component when in the pure state. It is defined by the relation

$$\left(\frac{\partial c}{\partial w_1}\right)_{w_2} = \bar{c}_1 \quad (X)$$

This says that the partial specific heat capacity \bar{c}_1 of component 1 in a mixture is defined as the rate of increase of heat capacity of the mixture with the addition of component 1, the amounts of the components being, for the purpose of this work, considered on a mass basis. There ^{are} corresponding expressions for the other components of the mixture. These derivatives, in the case of the mixtures studied here, may be obtained directly from the composition diagrams, Figures 6 and 7. The method used is called the "method of intercepts" and is described else-



MASS PERCENT PROPANE

FIGURE 8

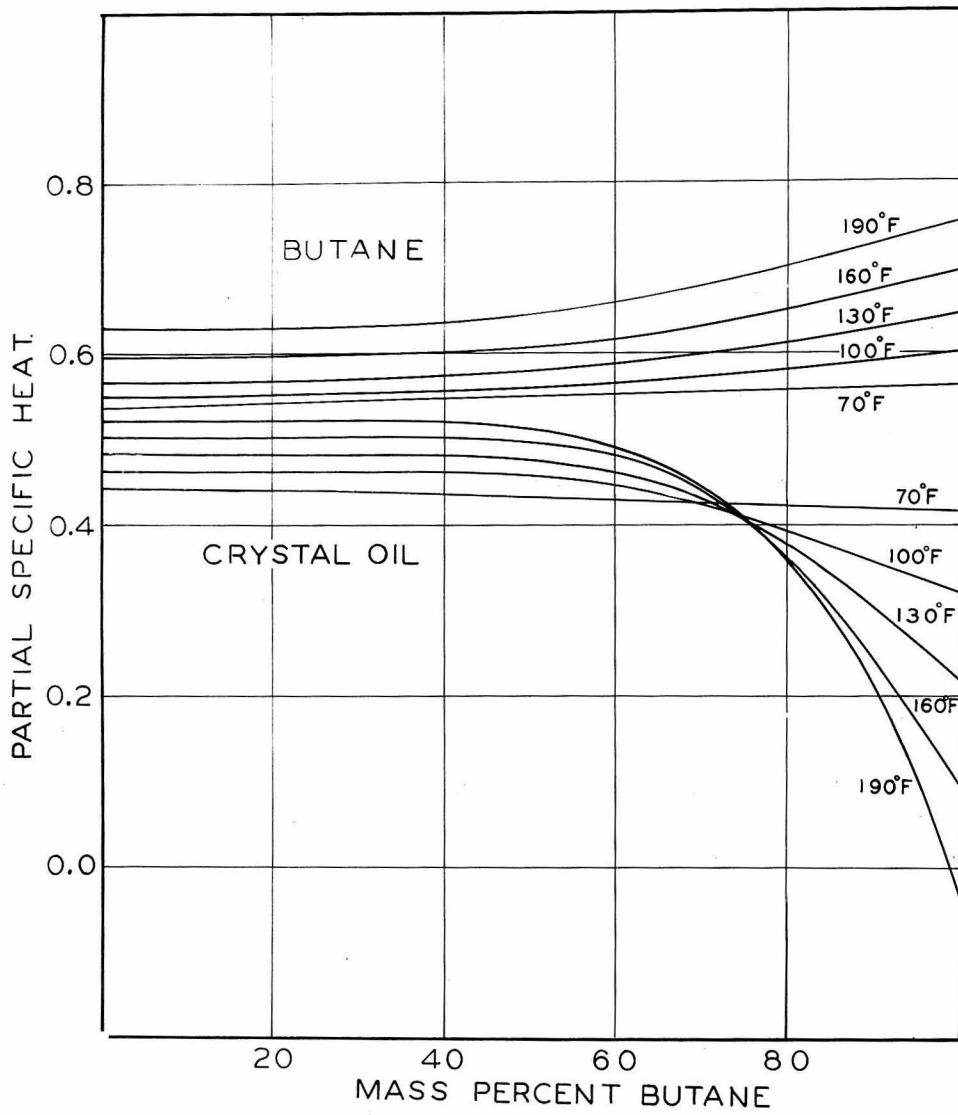


FIGURE 9

(4)
where . The results of a determination of such partial heat capacities for the propane and the butane mixtures are shown in Figures 8 and 9. The lower family of curves in each figure gives the partial specific heats of crystal oil, while the upper family is for propane and butane respectively.

Since hydrocarbons are relatively nonpolar substances, we might see how these quantities compare with those for the case when the mixtures behave as perfect solutions. In the latter case, the heat capacities would be strictly additive, and the derivative given above would be constant across the whole composition range, merely by definition of the additivity of properties. It will be noted that in the butane crystal oil system, the partial specific heats of both butane and crystal oil are practically constant up to about fifty mass percent butane. This means that within this range and for a given temperature, the specific heats of all the possible mixtures might be calculated a value for the constant partial for butane and one for crystal oil.

Such is not the case for the propane-crystal oil system. The partial specific heats are changing even in rather dilute concentrations of propane. For propane, however, the regularity lies on the other side of the diagram. Here the partial specific heat for propane is quite constant from 100% down to 50%, while the corresponding quantities for crystal oil increase by about 2 to 4% in this range.

Since these mixtures behave as perfect solutions within certain ranges, with respect to the property of

heat capacity, one might suspect that perhaps they also obeyed the laws of perfect solutions with respect to other properties. There is some evidence, based on data obtained in this laboratory, that the partial specific volumes for the butane-crystal oil system show the same characteristics as have been pointed out for the partial specific heats for this system.

In order to see whether these curves fulfill certain conditions required of all partial quantities, one may use the relation

$$\left(\frac{\partial \bar{c}_1}{\partial N_2}\right) / \left(\frac{\partial \bar{c}_2}{\partial N_2}\right) = -\frac{N_2}{N_1} \quad (\text{XI}) \quad (4)$$

where N_1 and N_2 are mass fractions of the components 1 and 2 respectively. In very dilute solutions of component 2, N_2 approaches zero. Then the ratio N_2/N_1 also approaches zero. This means that either the derivative $(\partial \bar{c}_1 / \partial N_2)$ is approaching zero, or that the other derivative is approaching infinity. For the case of heat capacities, the former holds. That this derivative is approaching zero means that in mixtures with high concentration of component 1, the change in the partial specific heat of component 1 with change in concentration is approaching zero, i.e., the curve comes in to zero concentration horizontally. This is clearly the case for mixtures low in butane, where the partial for crystal oil is quite flat. Also for propane mixtures low in crystal oil

the partial for propane is quite flat. For mixtures low in propane, the crystal oil partial is reasonably flat near zero, but for the last case--mixtures high in butane, this is so far from true that one is led to suspect that the absolute values for butane specific heat are a little too high. If such is the case, then a reconstruction of curves, using slightly lower values for butane, would change the slopes so much that the range in which the partials are constant would probably be extended considerably beyond fifty percent.

Corresponding to the case of simple additivity, the equation in the case when partial quantities are used is

$$N_1 \bar{c}_1 + N_2 \bar{c}_2 = C \quad (\text{XII})$$

where N indicates the mass fraction of the component; \bar{c} the appropriate partial specific heat; and C the resultant specific heat of the mixture. By the use of this equation and data such as presented in Figures 8 and 9, one is enabled to calculate the specific heat of any mixture in the system. Of course, the same thing could be done by direct reading off of Figures 6 and 7, but for the case of butane, the equation permits the evaluation of specific heats for mixtures up to 50% butane without the use of any graph at all. In the following Table 3 are listed the partial specific heats of the components for mixtures of butane and crystal oil, the values being those which are constant for all mixtures up to 50% butane.

Table 3
Partial Specific Heats

Temp °F	N-butane \bar{c}_p	Crystal oil \bar{c}_p
70	0.44	0.54
100	0.46	0.555
130	0.48	0.57
160	0.50	0.60
190	0.52	0.635

For any concentration with the range, mere substitution of these values in the equation (XII) will give the specific heat of the mixture to within about 2%.

It is interesting to speculate on the use of such observed partial quantities in other hydrocarbon mixtures. For instance, it is quite within the realm of possibility that the partial specific heat of butane or propane in crystal oil is approximately the same as that when they are dissolved in some other heavy hydrocarbon oil. The possibility of such a generalization would be interesting to investigate.

It should be said that interpretation of these partial specific heat diagrams must be made with caution. In diagrams like Figures 6 and 7, whenever the rate of curvature is high, the tangents which are constructed on them for evaluating the partial quantities are necessarily rather inaccurate. But, for the most part, the accuracy is

sufficient to warrant such conclusions as have been drawn here.

For the benefit of anyone who might wish to use the data here presented, a final remark should be made concerning C_p . It was defined as the specific heat at constant pressure for the liquid as a pressure just above bubble point pressure. This reference state was chosen because it was considered as the least arbitrary of the possible choices. Values of C_p calculated for this state also have the advantage that they are usable as values of C_p for the liquid in question at pressures a great deal higher than the bubble point pressure. The error made in using the values at higher pressures may be corrected or estimated by the equation

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial v}{\partial T}\right)_p \quad (\text{XIII})$$

Thus, for propane, a rather highly expansive liquid, at 100°F an increase of 200 pounds per square inch above the vapor pressure decreases the specific heat from 0.661 to 0.65. This is an extreme case, however, and the general difference for natural heavy hydrocarbon mixtures is much less. For n-butane, the next heavier member, this increase in pressure at 100°F will cause the specific heat to drop only from 0.601 to 0.598. Consequently, it may be seen that the values listed are quite usable over a wide range of pressures above bubble point pressure.

Summary

The specific heats of two series of liquid hydrocarbon mixtures have been determined. The components of one series were propane and crystal, a heavy, highly refined oil. The components of the second series were n-butane and crystal oil. The measurements were made as specific heats at constant volume for two phase mixtures, and these were converted to specific heats at constant pressure for the liquid. The results show that the specific heats of the components are not additive in the mixtures. However, by the use of the concept of partial specific heats, decided regularities in the two series were made apparent. On the basis of them, it was made possible to indicate a simple method for calculating the specific heats of butane-crystal oil mixtures.

Appendix

Typical Numerical Calculation

The case chosen is the mixture of propane and crystal oil, containing 73.33 mass % propane

Because of space limitations, the graphs which were used in these calculations cannot be shown, but the manner of their use will be indicated.

Calculation of specific heat at constant vol. for the system as it exists in the bomb

One point: voltage across the heater 6.084 volts
 current 0.2680 amps
 time 20 min.
 $Q = \text{energy input} = EIt = 32.62 \text{ watt-min.}$
 or 1.856 Btu

$$\begin{aligned} T_1 &= 95.808^\circ\text{F} \\ T_2 &= 107.144 \\ \Delta T &= 11.336^\circ \end{aligned} \quad \text{Mean } T = 101.5^\circ\text{F}$$

$$\frac{Q}{\Delta T} = \frac{1.856}{11.336} = 0.1637 \text{ Btu}/^\circ\text{F}$$

Heat capacity of the bomb taken from a dalibration curve at 101.5°F : $C_{\text{bomb}} = 0.0843 \text{ Btu}/^\circ\text{F}$

Heat capacity of contents = $0.1637 - 0.0843$
 $= 0.0794 \text{ Btu}/^\circ\text{F}$

Mass of contents = 61.182 gram = 0.1349 lb

$$C_v = \frac{0.0794}{0.1349} = 0.5886 \text{ at } 101.5^\circ\text{F}$$

Conversion of C_v to C_p just on the two phase side of the bubble point.

$$\text{The relation is } \left(\frac{\partial C_v}{\partial v} \right)_T = T \left(\frac{\partial^2 p}{\partial T^2} \right)_v$$

Now $\left(\frac{\partial p}{\partial T} \right)_v$ and $\left(\frac{d^2 p}{dT^2} \right)_{\text{sat}}$ are quite nearly equal in the two phase region, and as was noted in the discussion, this derivative does not vary appreciably with volume in the range of volumes considered. And so we may write

$$\Delta C_v = \left(\frac{d^2 p}{dT^2} \right)_{\text{sat}} (V_{\text{bomb}} - V_{\text{sat}})$$

From a graph of bubble point pressures vs composition are obtained values for the 73.33% mixture at a series of temperatures. These are shown in column II below. A plot of these against temperature gives a smooth curve on which tangents may be drawn, giving $\left(\frac{dp}{dT}\right)_{sat}$ shown in column III. In a similar manner, on a plot of $\left(\frac{d^2p}{dT^2}\right)$ against T, one obtains the second derivative shown in column IV

I	II	III	IV	V	VI	VII	VIII	IX
$T^\circ F$	P_{sat} psi	$\left(\frac{dp}{dT}\right)_{sat}$	$\left(\frac{d^2p}{dT^2}\right)_{sat}$	$T^\circ R$	V_{sat} cu ft/lb	$(V_{bomb} - V_{sat})$	$(V - V_{sat}) \times T \left(\frac{d^2p}{dT^2}\right)$	$C_v - C_{v,sat}$
70	123	1.80	1.66 $\times 10^{-2}$	530	.02495	.01724	.1517	0281
100	187	2.34	2.00	560	.02723	.01496	.1676	0310
130	267	2.98	2.38	590	.03038	.01181	.1672	0310
160	367	3.79	2.94	620	.03425	.00794	.1447	0268
190	502	4.187	4.00	650	.04025	.00194	.0504	0093

From a graph of saturation volumes against composition are obtained values for the 73.33% mixture at a series of temperatures, shown in column VI

Mass of sample = 61.182 gm = 0.1349 lb.

Volume of bomb = 161.2cc = 0.005692 cu.ft.

Sp vol of contents .005692 + 0.1349 = 0.04219 ft³/lb/

Subtracting from this the saturation volumes, we obtain column VII. Multiplying the values for $\left(\frac{d^2p}{dT^2}\right)$, T and $(V - V_{sat})$ all together gives the desired correction term, column VIII. To convert this term to heat units, we convert to foot-

pounds and then to Btu. Thus for the term at 70°

$$C_v - C_{v \text{ sat}} = 0.1517 \times 144 + 777.6 = 0.0281$$

Conversion from C_v on the two phase side of the bubble point to C_p on the one phase side.

The relation is

$$C_p = C_v + 2T \left(\frac{dv}{dT} \right)_{\text{sat}} \left(\frac{dp}{dT} \right)_{\text{sat}}$$

We already have values for $(dp/dT)_{\text{sat}}$, and also values for V_{sat} for the liquid. One plots V_{sat} against temperature and takes derivatives, shown in column III below.

I	II	III	IV	V	VI
$T^{\circ}F$	$\left(\frac{dp}{dT} \right)_{\text{sat}}$	$\left(\frac{dv}{dT} \right)_{\text{sat}}$ wt % / $^{\circ}F$	$T^{\circ}R$	$2T \left(\frac{dp}{dT} \right)_{\text{sat}} \left(\frac{dv}{dT} \right)_{\text{sat}}$	$C_p - C_v$
70	1.80	6.75×10^{-5}	530	0.1288	0.0239
100	2.34	8.80 ..	560	.2306	.0427
130	2.98	11.37 ..	590	.3998	.0740
160	3.79	15.54 ..	620	.7303	.1352
190	4.87	27.05 ..	650	1.7126	.3171

The next operation is simply to multiply the four quantities together $2 \times T \times \left(\frac{dv}{dT} \right) \times \left(\frac{dp}{dT} \right)$. Again, to convert this term to heat units, we multiply by $144/777.6$. values are shown in column VI.

$$\text{Thus for } 70^{\circ}, 1.80 \times 6.75 \times 10^{-5} \times 530 \times 2 = 0.1288$$

$$\text{and } 0.1288 \times 144/777.6 = 0.0239 = C_p - C_v$$

Applying these corrections to one case: For 70° , the smoothed value for C_v uncorrected is 0.568.

$$C_{v \text{ sat}} = 0.568 - 0.028 = 0.540$$

$$C_p = 0.540 + 0.024 = 0.564.$$

References

- (1) Bureau of Standards Paper No. 313
- (2) A convenient listing of these general functions
is given in Perry -- "Chemical Engineers' Handbook"
McGraw-Hill
- (4) Lewis and Randall "Thermodynamics" McGraw-Hill

Acknowledgement

The author wishes to thank the American Petroleum Institute and its individual members for their generous sponsorship of this research. For his clear-sighted advice and instruction in connection with this project, the author extends an admiring appreciation to Dr. W. N. Lacey. To Dr. B. H. Sage, for constant guidance in the rugged domain of thermodynamics and friendly co-operation in work, all my thanks.