

SOME STUDIES ON THE THERMODYNAMIC RELATIONS
IN MULTI-COMPONENT SYSTEMS

Thesis

By

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Up to the present time very little work has been done on the application of thermodynamics to liquid-gas multi-component systems. There are in existence many tables and charts giving the thermal properties of pure substances, but the only notable example of a chart for a mixture is the temperature-entropy chart for air.¹ Due to the fact that the critical temperatures of the main constituents of air are so close together, the chart for air is quite similar to that for a single component system. It does not show the critical phenomena peculiar to a mixture; nor does it show very clearly the difference in behavior in the two-phase region.

This thesis has been written with a view to presenting the thermal properties of a two-component system in which the critical temperatures of the components are sufficiently far apart to bring out clearly the properties peculiar to a mixture. A method is presented which employs simple thermodynamic relations to derive these quantities from complete pressure-volume-temperature data over the range studied, and from the change of one thermal quantity with temperature. The solutions have been obtained graphically, but could have been carried out analytically by fitting empirical equations to the pressure-volume-temperature data. This general method, which is valid for any multi-component system, no matter how complex, has been applied to the construction of a temperature-entropy chart for a fifty mol-percent mixture of methane and propane.

Sources of Data

From the pressure-volume-temperature data alone one can calculate, by means of rigorous thermodynamic relations, the isothermal changes in all the thermal properties of a system, but not the changes with temperature. To be able to refer the values of the thermal properties under any condition to a single arbitrary basis, one must know the change in one thermal quantity with temperature holding one physical condition constant (e.g. at one constant pressure or one constant volume). For this study, the data has been obtained from two sources. The pressure-volume-temperature data were taken from the data of Sage, Lacey, and Schaafsma on the methane-propane system.² Density data for the fifty mol-percent mixture were converted to volume data. When the experimental work was originally done, not much stress was placed on the low pressure region below about thirty atmospheres, with the result that the data were not reported to as many places, nor to as high an accuracy in this region as is required by thermodynamic calculations. Therefore the volumes at these lower pressures were calculated from compressibility factors $\left(\frac{pV}{p_1V_1}\right)$ by extrapolation of isotherms of these factors for the higher pressures to atmospheric pressure. The volumes were plotted as isobars on the temperature-volume plane, a portion of which is shown in Figure 1. C and C' are the critical and cricondentherm points. The point of maximum pressure occurs at about 40°C. The two-phase region is different from that of a pure substance in that the isobars are not horizontal. The thermal data consisted of an empirical equation for C_p for the lighter paraffins, taken from the literature.³ This equation

has been verified recently for propane,⁴ as well as for other paraffins and paraffin mixtures by various investigators.³ The equation is:

$MC_p = 4.4 + 4.4n + (0.012 + 0.006n)t$, where n is the number of carbon atoms in the molecule. In this case n equals 2.

Methods of Calculation

From Figure 1 values of $(\frac{\partial v}{\partial t})_p$ were obtained at a series of temperatures for each isobar by measuring the slope graphically. A plot was made of isotherms of these slopes against pressure. Figure 2 shows three such isotherms. The values of the slopes decrease with increase in pressure at constant temperature in the superheated region until close to the vapor dome. Near the vapor dome the isobars on the temperature-volume plane increase considerably in slope before entering the dome. This effect can be seen in Figure 2, where the 30° and 50°C isotherms double back on themselves in the superheated region. The slopes decrease almost as rapidly in the two phase region as in the superheated region. Between 80 and 90 atmospheres these two isotherms enter the condensed region with a sudden shift in slope. At the point of maximum temperature at a temperature between 30° and 50°C this shift does not occur. In the condensed region the slope decreases slowly. The slopes in the one phase regions behave similarly to those for a single-component system. In the two phase region the slopes in the latter case are, of course, infinite. The 70°C curve is above the cricondenthem temperature, but still shows the influence of the vapor dome. Figures 1 and 2 and the specific heat equation give all the values needed for the complete determination of all the thermal

properties within the range covered.

From thermodynamics comes the relation⁵ $(\frac{\partial v}{\partial t})_p = (\frac{\partial s}{\partial p})_t$. *
Hence integration of the area under the isotherms in Figure 2 will give the isothermal changes in entropy from some arbitrary pressure to any other pressure and to the two-phase boundaries. In the case of a pure substance this relation becomes indeterminate in the two-phase region. However, the Clapeyron equation can be used instead .

Another useful relation is given by the equation,
 $v = T (\frac{\partial v}{\partial t})_p + (\frac{\partial h}{\partial p})_t$ ⁵. By reading off the appropriate values from Figures 1 and 2, one can calculate $(\frac{\partial h}{\partial p})_t$ for a series of pressures at a number of temperatures and plot these values as isotherms against pressure. By integration of the area under these isotherms one can get the isothermal change in heat-content from some arbitrary pressure to any other pressure and to the two-phase boundaries. In this study both the change in entropy and the change in heat-content were calculated from one atmosphere, since the thermal data is given at this pressure.

The values of C_p were plotted against T, and a plot was also made of $\frac{C_p}{T}$ against T. The change in entropy and the change in heat-content at one atmosphere from 20°C to any other temperature could then be calculated by graphical integration of these two curves, since $ds = \frac{C_p}{T} dt$ and $dh = C_p dt$.⁵

The above calculations suffice to permit one to draw up a temperature-entropy diagram. The basis of such a chart is usually chosen as saturated liquid at some arbitrary temperature at the lower

* See page 11 for key to symbols used in this thesis.

end of the temperature range studied, the entropy and heat-content being called zero at this point. In this study the basis was chosen as saturated liquid at 20°C. Since the change in entropy with pressure was known at 20°C from the above calculations, the value of the entropy at the same temperature and at one atmosphere could be directly obtained. Knowing the change in entropy as a function of temperature at one atmosphere, a one atmosphere line could be drawn on the temperature-entropy plane, starting with the 20°C value. In like manner a one atmosphere line could be put on the heat-content temperature plane. Then the other constant pressure lines, as well as the two phase boundaries, could be put on both planes because the differences of entropy and heat-content from the one atmosphere values are known at a series of constant temperatures. The two phase boundary lines were rounded to meet at the tricritical temperature and the critical temperature was plotted. Constant heat-content lines were drawn on the temperature-entropy plane by transferring temperature-pressure intersections on the temperature-heat-content plane to the temperature-entropy plane. Figures 3 and 4 show the results of such plotting. The basis of these charts has been changed somewhat, as will be explained later, but the principles of their construction are still just as valid.

Lines of constant volume can also be put on the temperature-entropy plane by using the temperature intersections of the constant volume lines with the isobars in Figure 1. Unless there are a great many pressure lines, this method gives only a few points for each line, since the volume lines and the pressure lines have somewhat the same

slope on the temperature-entropy plane. More points can be obtained by plotting constant entropy lines on Figure 1 by transferring temperature intersections of the constant entropy lines with the isobars from Figure 3 to Figure 1. Two such lines are shown as dashed lines on Figure 1. Then temperature intersections of the constant volume lines with the constant entropy lines can be transferred to Figure 3 to give the necessary points. Another method of obtaining the constant volume lines is to draw isotherms on a pressure-entropy plane from points read from Figure 3. One can then find the entropy of each constant volume at a series of temperatures from the intersection of the equilibrium pressure for that volume and temperature with the corresponding isotherm. For a pure substance the volume lines in the two phase region are obtained from the relation $v_x = v_g + v_l(1-x)$ where x is the weight percent in the vapor phase.

Entropy and heat-content are not the only thermal quantities that can be obtained from such data as this. Having proceeded this far, one is in a very good position to calculate any of the other thermal properties of the system. For example, one can calculate the specific heat at constant pressure for any pressure and temperature in either one or two phase regions by measuring the slope of the pressure line on the temperature-entropy plane and applying the equation $\frac{C_p}{T} = \left(\frac{\partial s}{\partial t}\right)_p$. Similarly one can obtain the specific heat at constant volume or the specific heat of the saturated gas or liquid. The Joule-Thompson coefficient may be obtained from the relation $\mu = \left(\frac{\partial T}{\partial p}\right)_h$.

It must be remembered that the above method is applicable to any system whatsoever that is in equilibrium with its surroundings.

It could easily be applied to a complex mixture like a crude oil - natural gas system, or to a system in which solid phases occur. It is not limited to the case where the specific heat is a known function of temperature for one pressure in the gaseous region. One could just as easily apply a specific heat at either constant pressure or constant volume in the gaseous, two phase, or liquid region. One could use the Joule-Thompson coefficients if they were known as a function of temperature.

Discussion of Accuracy

In the construction of Figures 3 and 4, it was found that the basis originally chosen gave many negative values of the thermal quantities. Therefore the basis of the entropy values was shifted to 0.10 for saturated liquid at 20°C, and the basis for the heat-content values was shifted to 100 for the same conditions. It was then found that the portion of the chart including the liquid region and a part of the two phase region below 35°C gave results which were obviously incorrect. The heat-content lines recrossed the pressure lines, giving the peculiar effect of setting a lower limiting pressure below which a constant heat throttling could not occur. Similarly the pressure lines recrossed the entropy lines, thus setting a lower limit beyond which an isentropic expansion could not proceed. The calculations were rechecked and found correct. The abnormality can be explained by the lack of precise data at low pressures. Since the thermal values at higher pressures are based upon those at lower pressures, an error in these will throw off all the values at the same temperature. At the lower temperatures the vapor pressure was so low that none of the data in the gaseous region was as

accurate as was necessary for good thermal calculations. The compressibility curves at 20° and 30°C were drawn in largely by extrapolation, and probably the values thus obtained were inaccurate. From other calculations on this system and from comparison with charts for pure hydrocarbons it is believed that the error is in the direction of too small a change in the heat content and the entropy in the gas region at the lower temperature. Probably the saturated gas line should be much more vertical, which would push the saturated liquid line and the liquid region sufficiently to the left to remove the abnormal features.

It was not feasible to make further experiments to improve the data, so the lower left hand corner of the chart was omitted. This calculation points out the necessity of having good pressure-volume-temperature data, especially close to where the thermal data is taken. Errors in the experimental determination of thermal quantities will introduce a proportionate error in the final results. Errors in the pressure-volume-temperature data will cause larger errors in the isothermal changes in thermal quantities because the errors are accentuated by the process of taking derivatives.

Discussion of Results

Figure 3 is strikingly different from a temperature-entropy chart for a pure compound. The pressure lines in the two phase region are not horizontal as with a pure substance. Their extreme steepness is due to the great difference in critical temperatures of the two components. The highest temperature on the two-phase boundary is the cricondentherm, C' , while the critical temperature, C , lies considerably

lower and to the left of this point. The single phase region is very similar to that of a pure substance except near the critical region. The single phase gas region extends over on the left of the chart down to the critical temperature. This means that retrograde condensation will occur between the critical and cricondenthern temperatures. For instance, if the mixture in the state of a gas at one atmosphere and 50°C were compressed isothermally, it would start to condense at an entropy of about 0.22. The amount of condensate would at first increase and then decrease. At an entropy of 0.105 the mixture would be completely gaseous again, since it would enter the single phase region above the critical temperature. Pressure lines in the liquid region below 90 atmospheres enter the two phase region. 90 atmospheres is the maximum pressure at which two phases of this mixture can exist in equilibrium and a 90 atmosphere isobar would just be tangent to the two phase boundary. An 88 atmosphere isobar would pass through the critical. Between the critical pressure and the maximum pressure one would also have retrograde condensation. If the temperature were raised along an 89 atmosphere isobar the mixture would first start to vaporize and would then condense again and enter the liquid region a little below the critical point.

Thermal charts for the usual crude oil-natural gas systems under the same conditions of temperature and pressure would be considerably different because the critical region would fall far above this temperature range. Also, the two phase region would extend to pressures far below atmospheric because of the very low vapor pressures of some of the constituents of the crude oil. The lines in the liquid region would be much more parallel and evenly spaced, as would be the case for the mixture of

methane and propane at temperatures far below the critical.

The slopes of the heat-content lines in the liquid region of the methane-propane mixture change in sign from negative to positive at sufficiently high pressures, so that a constant heat-content expansion would result in a rise in temperature. The inversion of this Joule-Thompson effect comes closer and closer to the two-phase boundary as the temperature is lowered. With a crude oil-natural gas system at temperatures far below the critical, one would probably not even notice this inversion, since it would occur so close to the two-phase boundary.

From this study several conclusions can be drawn. In the first place the original data used in such calculations must be of a high degree of accuracy. The calculations involved are somewhat tedious, but are perfectly straightforward and involve no assumptions. Such calculations might be employed advantageously with other data to put them in a more useable form and to derive values of many useful properties which would otherwise not be available. Although the particular data here presented is not of very much practical significance, a series of similar charts covering a range of compositions for a series of hydrocarbon systems would be of very great value in solving many of the problems occurring in production and refining.

List of Symbols

- p Pressure on system in standard atmospheres (760 mm.)
- v Volume in cubic centimeters per gram.
- t Temperature in degrees centigrade.
- T Temperature in degrees Kelvin.
- s Entropy in calories per gram per degree Kelvin.
- h Heat-content in calories per gram.
- C Heat capacity in calories per gram per degree centigrade..

References

- 1 Hausen, Der Thomsen-Joule Effekt
- 2 Sage, Lacey, and Schaafsma, Ind. and Eng. Chem. 26, 214 (1934)
- 3 Lewis and MacAdams, Chem. and Met. Eng., 436 (1929)
- 4 B. H. Sage, Ph.D. Thesis, California Institute of Technology (1934)
- 5 Lewis and Randall, Thermodynamics and the Free Energy of
Chemical Substances, pp. 132, 133, and 134.

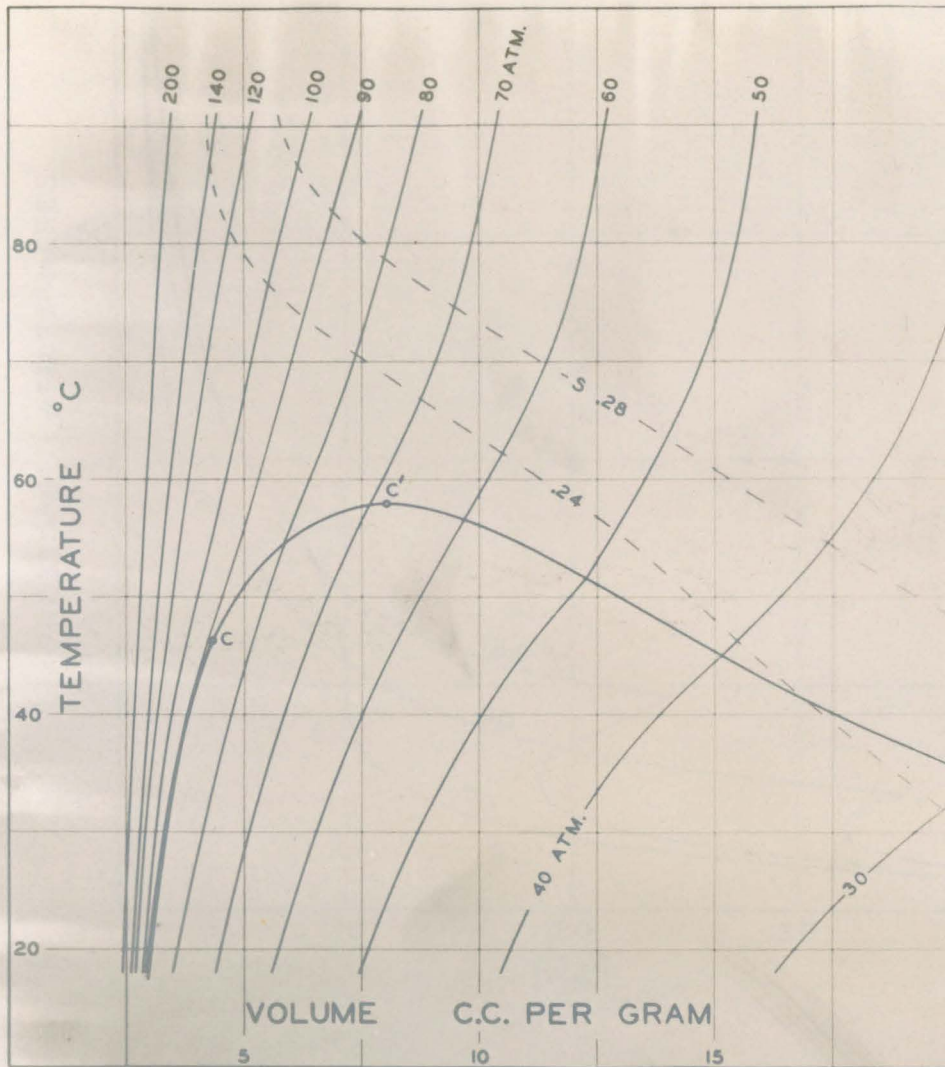


Figure 1

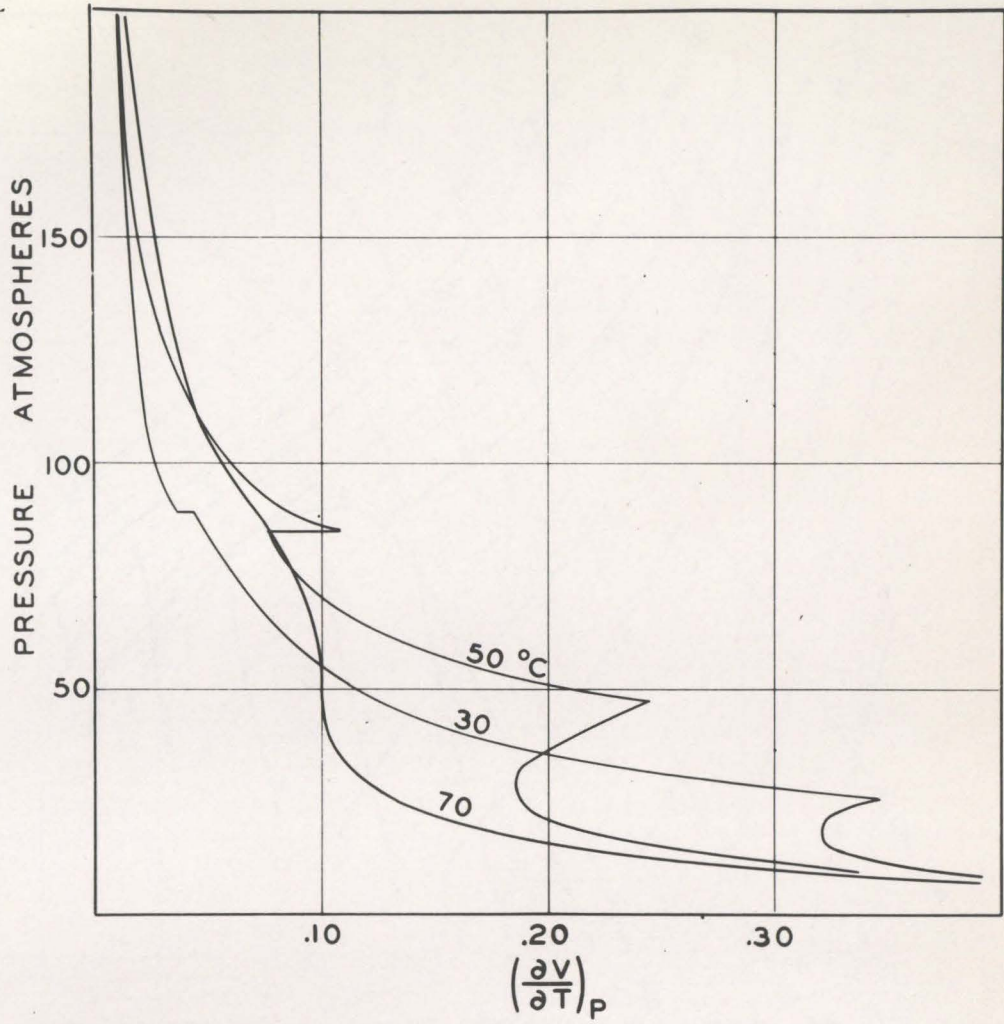


Figure 2

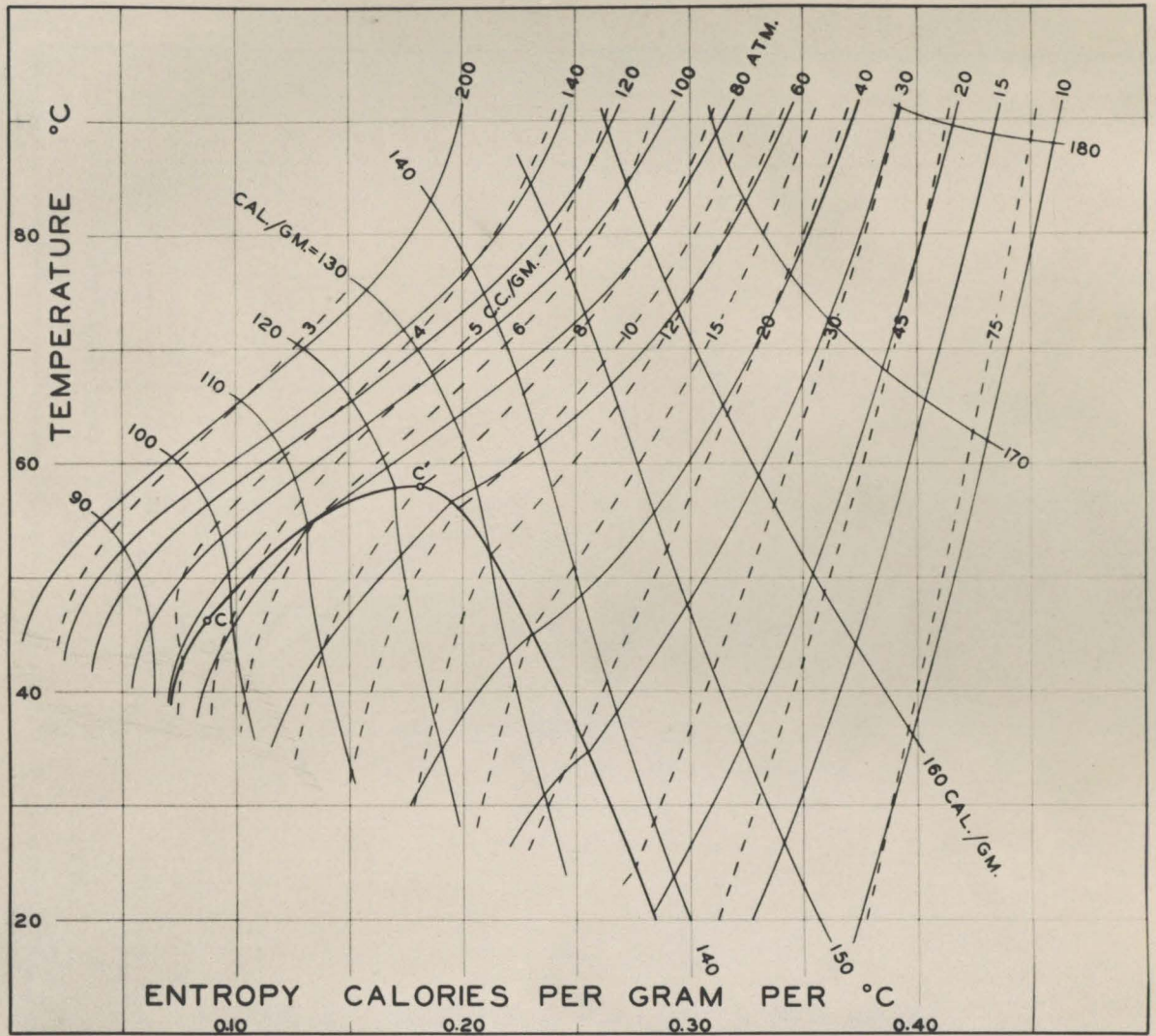


Figure 3

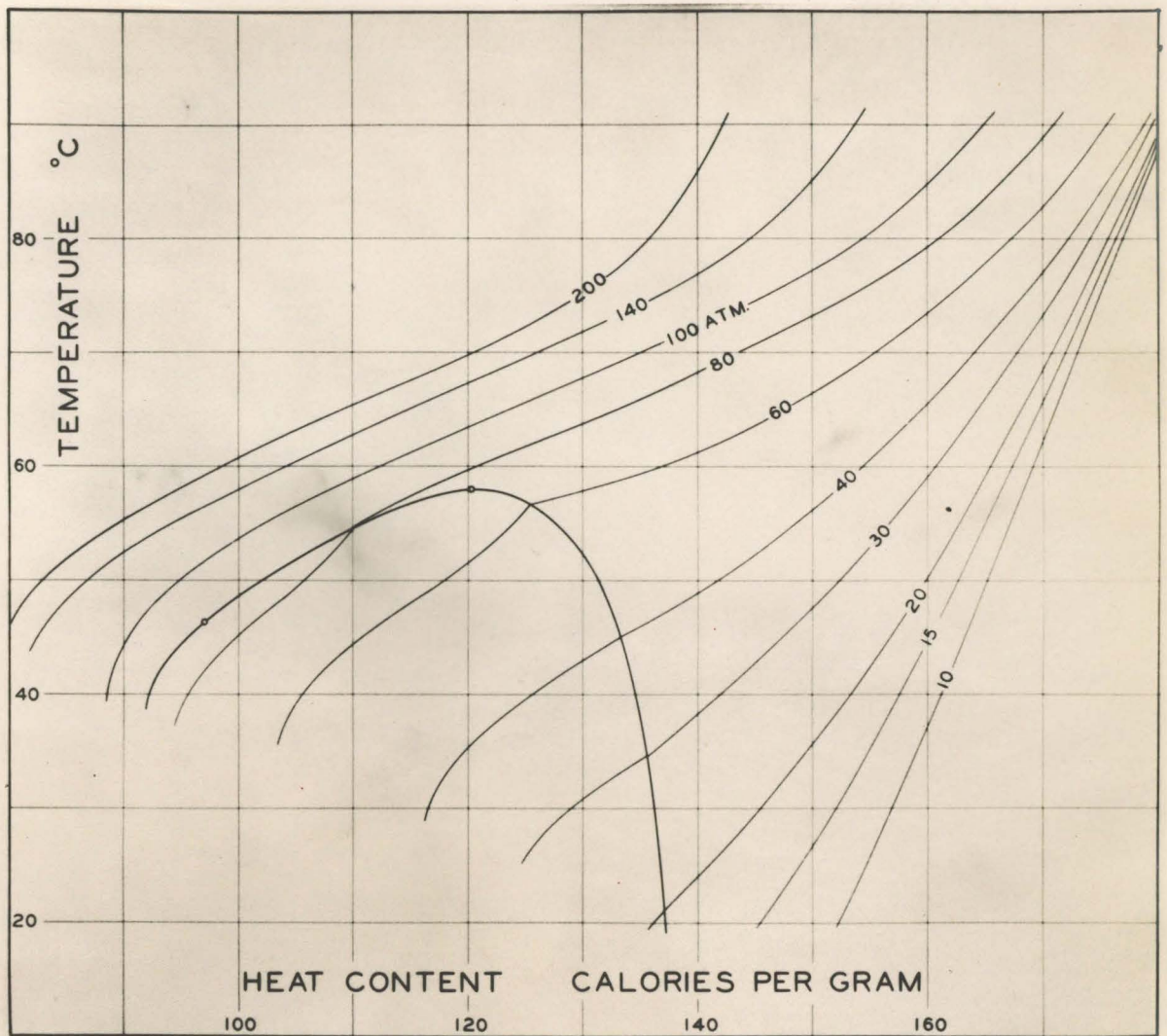


Figure 4