SCHOOL OF ENGINEERING
DEPARTMENT OF MECHANICAL ENGINEERING

January 19, 1977

Dr. Howard T. Hall
P.O. Box 7533
University Station
Provo, Utah 84602

Dear Dr. Hall:

I have enclosed one copy of our proposal and attachments which had been funded by NSF. Also included is a set of detail drawings of the test apparatus which we have built and two photographs to show the critical components.

We would appreciate you reviewing this material and critiquing the design. Mr. Kurt Rolle will be in Provo, Utah, on March 1, 1977 at 1:30 p.m. to discuss the design with you. We specifically would like your input regarding the overall design of the device for the pressure range to 30,000 atm pressure and 0-70°C. Also, we would like guidance for 1.) reducing or accounting for friction in the test section 2.) encapsulation of liquid test material and 3.) removal of gasses from the liquid samples. We are using an LVDT to sense volume changes and MTS machine to apply the loads. Also, we are developing a computer program to allow us to account for any "barreling" of the test specimen. This correction could provide more accurate volume measurements. Your reaction to any of these arrangements would be most welcome at this initial phase of our work.

If there are any specific questions you may have regarding this program please feel free to call me any time.

Very truly yours,

John N. Crisp
Associate Professor

JNC/mlo

Encl.

UNIVERSITY OF DAYTON
DAYTON, OHIO 45469

SCHOOL OF ENGINEERING
DEPARTMENT OF MECHANICAL ENGINEERING

May 14, 1976

Dr. Marshall M. Lih, Program Director
Thermodynamics and Mass Transfer
Division of Engineering
National Science Foundation
Washington, D. C.   20550

Dear Dr. Lih:

Thank you for giving us the opportunity to respond to the reviewers' comments.

I have attached our response accordingly. Should you need any other information please don't hesitate to contact me.

Very truly yours,

John N. Crisp

John N. Crisp
Associate Professor

JNC:cr
Att.

Supplement to Research Proposal

Submitted to the National Science Foundation on

"THE EXPERIMENTAL DETERMINATION OF THERMODYNAMIC

EQUILIBRIUM DIAGRAMS FOR LUBRICANTS"

Latest Publications

This proposal was written to seek support in an area heretofore not investigated by others. We conducted an extensive literature search and a library research. We are, of course, continually seeking information to determine the extent of knowledge relating to the specific equilibrium phase diagrams for synthetic lubricants or natural lubricants. We are unaware of any work being done or funded which is concerned with the range of P-V-T data we are proposing.

The Air Force program at Rensselaer Polytechnic Institute, to the best of our knowledge, is considering the dynamic mechanical properties of lubricants in the range of pressures up to 250,000 psi and temperatures to 150°F. The equilibrium phase diagrams are not expected to be fully developed. This proposal seeks to determine the static, equilibrium states of synthetic lubricants over a pressure range to 500,000 psi and temperature to 160°F, as well as identifying the precise phases existing at the various states.

The work at the Catholic University of America, funded by ONR, is concerned with the visco-elastic properties and other dynamic properties of lubricants. The work is being done for low-pressure, low-temperature applications. Phase diagrams will be only a peripheral concern.

Georgia Institute of Technology has recently received a source of funds from NASA to determine phase changes to 140,000 psi. This work is a natural continuation of the fine work done at Georgia Tech in seeking viscosity

relationship with temperature and pressure.

While there is certainly some overlapping of the ranges of interest of these programs, the emphasis on static equilibrium conditions to very high pressures and the identification of distinct phases appears to be unique. Additionally, this information would provide a significant amount of knowledge for science and technology.

Phase Rule

We agree with the reviewer regarding his comments pertaining to the phase rule. In reviewing our comments in the proposal, as the reviewer correctly noted, we should have pointed out that for two phases in equilibrium there is only one independent intensive property which fixes the state of each phase. What we intended to say, however, was that when temperature and pressure are held constant during the phase change the average value of the properties of the mixture depend, for example, on the total volume (a third property).

Therefore, in our research we intend to monitor pressure, temperature and volume. The detection of phase changes will, in fact, be determined for the most part, from an analysis using these three properties. The method was well established by Bridgeman and others as cited in our proposal.

X-ray Diffraction Analysis

The primary phase changes anticipated in this program are liquid to solid. As lubricants solidify the transition may be to an amorphous or a crystalline solid. There is the possibility that some crystalline characteristics may be present or that the solid may be fully crystalline such as occur for example with silicones.

2.

As this research is concerned with the identification of the phases existing at various equilibrium states it was felt that any of the analytic techniques available that might further identify the phases present whould be considered. Thus x-ray diffraction, for example, could conceivably be used to ascertain the extent or degree of the crystalline structure present.

Accuracy of Measurements

The Clapeyron equation provides a means for calculating the difference in enthalpy of two phases in equilibrium at the phase change. This difference is called the latent heat of solidification for liquid-to-solid phase changes. The Clapeyron equation involves the differentiation of pressure with respect to temperature and on a P-T plane of an equilibrium diagram. This is simply the slope of the phase boundary. Thus, as shown in Figure 1 for a typical P-T diagram at the temperature T^*, the latent heat of solidification can be readily measured as the slope of the curve dP/dT. It is certainly true that accuracy in data collection is critical in determining the P-V-T relationships and equally so for obtaining slopes of phase boundaries
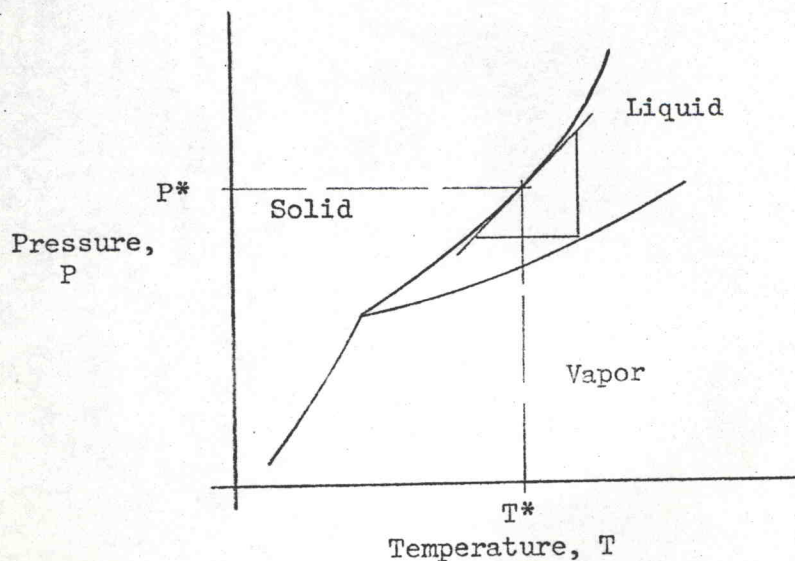

Figure 1 - Typical Pressure-Temperature
Equilibrium diagram of Pure Substance.

We did not intend to slight the error analysis of the test program. Since we are basically employing techniques used by P. Bridgeman to determine phase transitions, as discussed in our proposal, it is hoped that we can improve on the accuracy obtained by Bridgeman. This should be possible using state-of-the-art measuring techniques.

Our preliminary error analysis for evaluation of the errors associated with the determination of equilibrium phase diagrams of lubricants was as follows:

The volume of lubricant V will be determined by measuring the test specimen diameter D and length L as discussed in the proposal. The volume is given by

$$V = \pi D^2 L / 4 \tag{1}$$

The error in volume is given by

$$\Delta V = \frac{\partial V}{\partial L} \Delta L + \frac{\partial V}{\partial D} \Delta D \tag{2}$$

which becomes

$$\Delta V = \frac{\pi D^2}{4} \Delta L + \frac{\pi D L}{2} \Delta D \tag{3}$$

Similarly the error in cross sectional area A is given by

$$\Delta A = \frac{\pi D}{2} \Delta D \tag{4}$$

The pressure P is given by

$$P = \frac{F}{A} \tag{5}$$

and the error in pressure is

$$\Delta P = \frac{\Delta F}{A} - \frac{F}{A^2} \Delta A$$

$$= \frac{4 \cdot \Delta F}{\pi D^2} - \frac{8F}{\pi D^3} \Delta D \tag{6}$$

The measured errors from the various equipment capability are estimated at

$$\Delta L \approx \pm .0001 \text{ in.}$$

$$\Delta D \approx \pm .0001 \text{ in.}$$

$$\frac{\Delta F}{F} = 0.1\% \text{ (of full scale)}$$

$$\frac{\Delta T}{T} = 0.1\% \text{ (of full scale)}$$

The full scale values associated with the measuring equipment are

$$T_{max} = 200°F$$

$$F_{max} = 60000 \text{ lbs.}$$

Thus

$$\Delta F_{max} = 60 \text{ lbs.}$$

$$\Delta T_{max} = 0.2°F$$

Using anticipated test values of D = .250 in., L = .375 in., (corresponding to P = 500,000 psi), T = 160°F and estimated measuring errors the maximum errors expected from the test apparatus, for example, from equations 3 and 6 are

$$\Delta P \approx 1600 \text{ psi}$$

$$\Delta V \approx 2 \times 10^{-5} \text{ in.}$$

and the percent error expected is

$$\frac{\Delta P}{P} \approx 0.3\%$$

$$\frac{\Delta V}{V} \approx 0.1\%$$

$$\frac{\Delta T}{T} \approx 0.1\%$$

The confidence, or accuracy, in a particular state being described by a given set of data, P-V-T, then will lie in a cubic volume of the P-V-T mapping having sides of 0.3%, 0.1% and 0.1% respectively as shown in Figure 2.
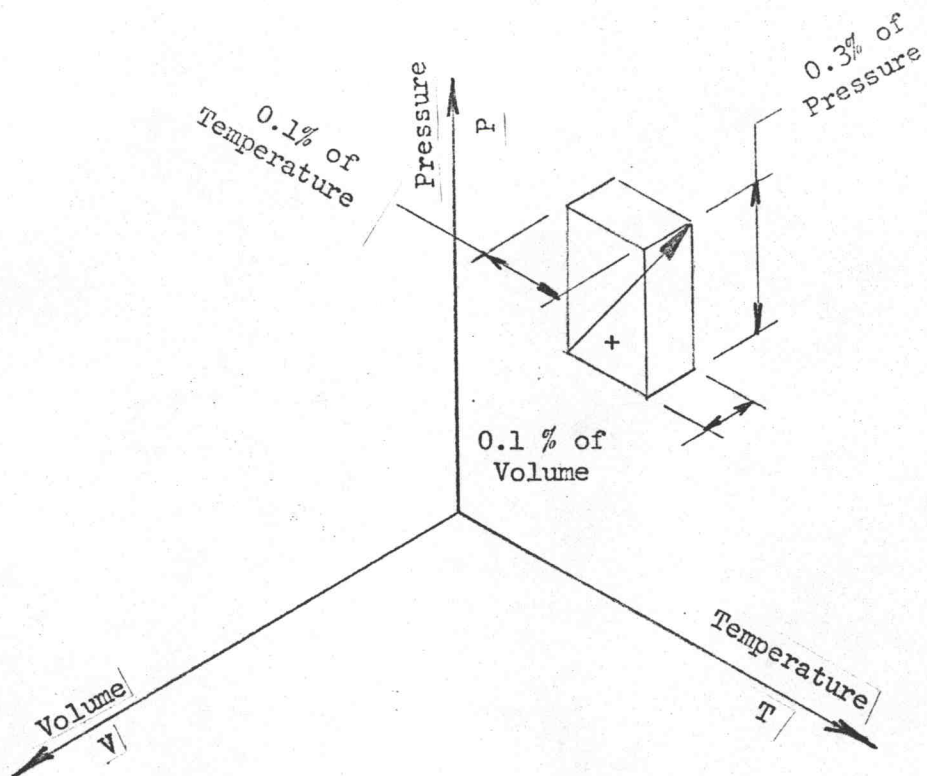
Figure 2 - Errors in a P-V-T mapping
of an Equilibrium State.

In determining the slope of a phase change locus a series of states must of course be given or determined. The maximum error occuring from such extraction requires an analysis of the relative accuracy of succeeding points. The error in the determination of each point should be less than the diagonal of the parallelpiped shown in Figure 2. We estimate this error to be approximately 0.33%.

The foregoing analysis is intended only as a preliminary error analysis. It is anticipated that as the test program progresses we will be able to improve the accuracy of the measurements beyond that discussed above. In any test program a more complete error analysis will be conducted and included as part of the final report.

Scope of Proposed Research

The research plan which describes the phases and results which will be produced is given on page 5-2 of the proposal. The thermodynamic equilibrium diagram, heats of transitions and changes in chemical structure will be obtained for a typical lubricant with a diester base, a lubricant with a polyester base and a lubricant with a polyphenolether base. These results will be obtained for a temperature range of 32°F to 168°F and a pressure range of 100,000 psi to 500,000 psi. A substantial number of tests will be run with each lubricant to insure repeatability.