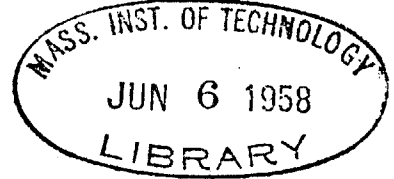


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SOLID-LIQUID EQUILIBRIA OF  
THE METHANE-ETHANE SYSTEM

by



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Submitted in Partial Fulfillment  
of the Requirements for the  
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## I. SUMMARY

The object of this thesis is the investigation of solid-liquid equilibria in the methane-ethane system. The initial freezing point of different methane-ethane mixtures was determined by observation of the mixture in an equilibrium flask. The quantities of methane and ethane present in the flask were determined beforehand by placing the pure gases, one at a time, in a large container and calculating the number of moles present from P-V-T relations. The temperature was measured with a copper-constantin thermocouple.

Results show the formation of almost perfect mixtures in the equilibrium flask. The theoretical eutectic composition is 0.662 mole fraction methane at  $-204.2^{\circ}\text{C}$ .

The apparatus employed was well suited for study of solid-liquid equilibria of mixtures at very low temperature and pressure.

## II. INTRODUCTION

### I. Purpose

The purpose of this investigation was to develop a suitable apparatus for use in studying low temperature solid-liquid equilibrium, and to study solid-liquid equilibria of the methane-ethane system.

### 2. Theoretical

When a liquid mixture of two components solidifies, one of three things may happen:

1. Pure crystals of the major or minor component may freeze out.
2. A solid solution may freeze out.
3. A eutectic mixture may solidify.

A solid solution is a homogeneous solid in which molecules of each component are in an ordered crystal lattice or randomly mixed throughout the solid. It has a definite melting point which may be higher or lower than either of the pure components.

A perfect mixture is a solution which has no solid compounds formed. The minor component depresses the freezing point of the major component the same as a salt depresses the freezing point of water. The major component solidifies in the pure state. When the freezing point depression reaches its maximum value both components freeze out simultaneously leaving a solid containing minute separate crystals of each component. The composition of this solid is called the "eutectic composition".

It is theoretically possible to predict the freezing point lowering effect of a minor component in a mixture. The calculation is based on the fact that at equilibrium the free energy of the solid formed is equal to the free energy of the liquid in contact with it. Thermodynamically, the freezing point lowering is dependent upon,

1. the heat of fusion of the pure component freezing out.
2. the activity of the major component in the solution.

The following relationship holds:

$$\ln a_1 = \frac{\Delta H_{\text{fusion at } T_f} (C_{pl} - C_{ps}) \Delta T}{RT_f^2} \quad (1)$$

It is impossible to accurately predict the formation of solid solutions. The formation of solid solutions depends upon the geometry of the molecules involved, as well as the energies of fusion. By examining mixtures of compounds and observing their freezing points, it is possible to get ideas about the structure of the individual molecules by studying the composition of solid solutions, if formed.

A study of the freezing points of methane-ethane mixtures in this experiment will give an indication of the types of solids formed. These studies are conducted at some value near the triple point of methane and ethane, which are almost identical (  $-182^\circ \text{C}$ . and about 20 mm Hg).

## II. INTRODUCTION (Cont.)

### 3. State of the Art

Up to the present time, little work has been accomplished

in the field of liquid-vapor equilibria of the various hydrocarbons at low temperatures.

In 1939, Ruheman (4) studied the vapor-liquid equilibria of the methane-ethane system at temperatures from  $-104^{\circ}$  to  $0^{\circ}$  C. and pressures up to 100 atmospheres. The phases were analyzed by a catharometer which is based on the principle of thermal conductivity differences between the components. In 1942, Levitskaya (3) studied the same system at similar temperatures and pressures.

In 1949, Sage and Hough (5) continued work on the ethane-methane system by obtaining equilibrium data at temperatures from  $38^{\circ}$  to  $121^{\circ}$  F. and pressures up to 204 atmospheres. Since 1949 however, no work has been carried out concerning vapor equilibria in the methane-ethane system.

In 1950, Clark and Din (2) were the first to investigate solid-liquid equilibria of hydrocarbons at low temperature. They investigated the systems, ethylene-ethane, acetylene-ethylene, and acetylene-ethane and found that the system acetylene-ethylene formed a solid solution. They employed volumetric methods to measure the amount of each gas present in the system before mixing, and from the data obtained, the composition of the mixture was calculated. Since their initial investigations, nothing has been accomplished on the study of low temperature solid-liquid equilibrium in hydrocarbons.



## II. INTRODUCTION (Cont.)

### 4. Apparatus

In designing a suitable apparatus for the investigation, the following points were kept in mind;

1. The apparatus should be suitable for low temperature work.
2. The apparatus should be simple in design and easy to construct.
3. The apparatus should allow the system to reach an equilibrium state rapidly and accurately.
4. The apparatus should be simple in operation allowing rapid experimental technique.

In consideration of the above requirements it was necessary to choose methods of:

1. determining the various compositions of the methane-ethane mixture.
2. determining how the temperature was to be measured.
3. determining how the data were to be gathered.

In the past the following methods have been used to determine the ratio of different compounds present in hydrocarbon systems:

1. Analysis technique based on chemical reactivity differences of the components.
2. Techniques that make use of differences in physical properties. Two examples are density or mass, and thermal conductivity differences.

3. Techniques that measure the amount of each component present and then mix them. Measurements of amounts present can be made by weighing or determining quantities from P-V-T relations.

In this thesis the third method of analysis was employed for the following reasons:

1. Methane and ethane are very similar chemically which makes it difficult to accurately distinguish between them by chemical analysis.
2. The apparatus needed to measure certain physical properties of methane and ethane mixtures is complicated and beyond the scope of this work.
3. In using the volumetric method it is possible to work near atmospheric pressure and temperature while measuring the amounts present. This eliminates the need for complicated and elaborate pressure or cooling equipment.

In nearly all previous studies of low temperature equilibrium, the copper-constantin thermocouple was used with high accuracy and convenience. This type of thermocouple was employed in the investigation.

It was possible to control the rate of heat removal from the methane-ethane system, slightly above the freezing point by employing an equilibrium flask that is insulated from liquid nitrogen by a vapor space of nitrogen gas. By adjusting the amount of nitrogen in the container, or by

adjusting the equilibrium flask's position in relation to the liquid nitrogen, it was possible to adjust the rate of cooling.

Solid formation in the mixture during cooling was observed through the wall of the equilibrium flask. Potentiometer readings were obtained at the first visual sign of solid formation.

#### 5. Equipment and Materials

Figure 1 is the flow sheet of the apparatus. All tubing and valves employed are of thick walled glass with an internal diameter of 7 mm. Connections are made with heavy wall rubber tubing. A needle valve is employed to control gas flow from the commercial cylinder. The vacuum pump was capable of maintaining a vacuum of 0.1 mm. Hg. The stirrer employed agitated the entire equilibrium flask to insure even cooling.

The methane and ethane gas employed is classified "technical grade" and has a minimum purity of 95%.

### III. PROCEDURE

#### 1. Experimental

The apparatus used employs the following principles:

1. A volumetric method of determining composition of the methane-ethane mixtures.
2. A thermocouple to measure temperatures in the equilibrium flask.
3. A method of performing the experiments at near atmospheric pressure.

The step by step experimental procedure followed was:

(valves are numbered on Figure 1:)

1. An ethane commercial gas cylinder is fastened to needle valve three, which is closed.
2. Valve two is closed. Valves one, five, and four are opened.
3. A vacuum is drawn on the system until there is no change in the manometer readings with time. Valves one, four, and five are closed.
4. The precondensing flask is placed in liquid nitrogen.
5. Needle valve three is cracked and ethane gas is allowed to condense in the precondensing flask. Approximately 200 ml. of liquid is allowed to collect, in the flask. Valve three is closed.
6. Valve four is opened and a vacuum again drawn. About 25 to 50 ml. of liquid ethane is allowed to "boil" off through the vacuum pump. Valve four is closed.

7. Valve one is opened and the liquid nitrogen removed from about the precondensing flask. The liquid is allowed to "boil" off into the storage cylinder. Equilibrium is established by waiting about 10 minutes. The pressure and temperature in the storage cylinder is recorded.
8. Valve five is opened. Liquid nitrogen is placed around the equilibrium flask. Gas is allowed to condense in the flask until equilibrium is established. Valve five is closed. The pressure and temperature in the storage cylinder is recorded. The contents of the equilibrium flask are frozen.
9. Valve four is opened. A vacuum is drawn. Valve four is closed.
10. Gas cylinders are switched; methane replacing ethane. Liquid nitrogen is placed around the precondensing flask. Valve three is opened. Gas is allowed to condense in the precondensing flask until approximately 200 ml. accumulate. Valve three is closed.
11. Valve four is opened. A vacuum is drawn until about 25 ml. of liquid methane "boils" off through the vacuum pump. Valve four is closed.
12. Valve one is opened. The liquid nitrogen is removed from about the precondensing flask and the liquid is allowed to "boil" off into the gas storage cylinder. Valve one is closed. Valve four is opened and a vacuum drawn. Valve four is closed.

13. The pressure and temperature in the storage cylinder is recorded.
14. Valves one and five are opened and methane is allowed to condense in the equilibrium flask until the pressure of the storage cylinder decreases approximately 10 cm<sup>Hg</sup>. Valve one is closed and the pressure and temperature in the storage cylinder is recorded.
15. The liquid nitrogen level around the equilibrium flask is lowered until the mixture melts. The stirrer is then turned on. The level of the liquid nitrogen is raised and cooling is allowed to proceed until the first signs of solid formation are observed through the walls of the flask. The potentiometer reading is then recorded. The cooling process is repeated twice to be sure that the potentiometer reading is as accurate as possible. The contents are then frozen.
16. Valve one is opened and the pressure in the storage cylinder allowed to drop another 10cm. increment. Valve one is closed and the pressure and temperature recorded.
17. The cooling process is repeated in the equilibrium flask for four or more increments.
18. After the last run, valve two is opened and the solution allowed to boil off to the atmosphere.

19. Steps one through eighteen are then repeated except that the methane and ethane cylinders are switched.

Gas is allowed to "boil" off through the vacuum pump during the experiment to remove the volatile components in the gas. After initial condensation of the gas, the pressure in the system is higher than that predicted from the vapor pressure of pure ethane alone. Removal of the volatile components contributes to the accuracy of the experiment by increasing the purity of the gas.

#### IV. RESULTS

Values of potential versus temperature for the copper-constantin thermocouple are plotted on Graph four. The curve is extrapolated to the liquid nitrogen temperature. (8) The reference temperature is  $-195.8^{\circ}\text{C}$ . at a potential of 5.505 millivolts. A line parallel to the standard curve through this point is constructed. Values of temperature in the equilibrium flask are determined from this line.

Mole fraction methane is calculated from the pressure data and this is plotted versus temperature on graph one. Plots of  $\ln$  mole fraction ethane or methane versus  $\Delta T$ , (freezing temperature of pure component,  $T_p$ —freezing point of the mixture,  $T_f$ ), are found on graphs three and four. The lines drawn on graphs one, two, three, and four are those calculated by theory, and therefore, a visual comparison of the data with theory may be made.



## V. DISCUSSION OF RESULTS

The apparatus and the conditions of the experiment give the data an excellent degree of accuracy for the following reasons:

1. The accuracy of the potentiometer is very high. The instrument employed had a resolution of  $\pm 1$  microvolt. The degree of resolution was higher than the experimental conditions demanded.
2. The thoroughness of stirring maintained the equilibrium flask temperature very uniform. This was witnessed from the fact that while stirring there was very small, if any, fluctuation in the potentiometer reading.
3. The purity of the starting materials was such, that the freezing point of the pure component was only about  $2^{\circ}\text{C}$ . lower than the temperature given in the literature (6).
4. The basic theory of measuring the amounts of gas present by P-V-T relations was good. High accuracy could be obtained with minimum skill in laboratory technique.
5. At the first sign of solid formation, the potentiometer ceased its movement for a few seconds. The potential was recorded at this point. By taking the potential reading at a constant value, the accuracy of reading the voltage scale was undoubtedly increased.

However certain conditions existed that had to be

carefully controlled to insure accurate data. These conditions were:

1. The formation of fog on the equilibrium flask. Water vapor was continually condensing on the equilibrium flask and forming ice crystals there. The flask had to be raised out of the liquid nitrogen and cleaned several times during a run. The fog made it difficult to determine the point of solid formation in some cases.
2. The effect of the precondensing flask on the storage cylinder volume. This effect was very small and for the most part eliminated under the conditions of the experiment. However, while performing a run there was a certain amount of vapor in equilibrium with the solid-liquid solution. This vapor was most likely of different composition than the liquid. Although the errors caused by this situation are small, they exist and are amplified by the presence of the precondensing flask.
3. Supercooling effects may be taking place. The degree of supercooling is an important consideration. The potentiometer indicated an increase in the temperature of one or two degrees centigrade after initial solidification in a few runs. This effect must be remembered in the interpretation of the results.
4. The thermometer measuring the temperature of the gas in the storage cylinder was strapped to the outside

of the container and covered with an insulating material. Readings of the temperature therefore, assumed that the gas inside the cylinder was the same temperature as the cylinder wall. In some cases this may not be true when the temperature was recorded soon after the gas was placed in the cylinder. However, care was exercised in checking to see that there were no rapid fluctuations after recording a temperature.

5. The impurities in the initial components would cause a freezing point lowering of the mixture. However, the data obtained were compared against the freezing point of the initial slightly impure gas, in hopes that the freezing point lowering due to impurities would be a constant value and therefore, cancel out when plotted against this reference point. In actual practice however, the freezing point lowering would effect the theoretical values as these are determined from data that were based on a different freezing point. Corrections were made to very nearly cancel this effect.
6. Errors associated with experimental technique. The possibility of very small leaks in the vacuum system, or of adsorbed gases on the walls of the storage tank that were somehow removed to the equilibrium flask, and associated phenomena must all be taken into consideration as possible sources of error. However, the data indicate that these errors were small

or did not exist at all.

In general it may be safely stated that the data points obtained were all in the region of experimental error when compared against theoretical calculated values that assume a perfect mixture.

The data points calculated from observation indicate a greater freezing point lowering than that calculated by theory. This discrepancy is indicative of the following types of error.

1. Supercooling effects which may lower the true temperature two degrees centigrade.
2. Errors involved in the calculation of the theoretical points when using the freezing temperature of the impure initial gas as a reference point.
3. The formation of fog that hinders observation of the initial solid and hence allows solid to accumulate and lower the temperature ~~of the system~~ before the solid is observed experimentally.

The effects of one and three above are probably the major source of error in the experiment. The fact that these types of error tend to increase the  $\Delta T$  (or increase the freezing point lowering), and that the data deviate in the same manner is indicative of reasonable data. Therefore, the methane-ethane system does form perfect mixtures over the range of conditions studied.

## VI. CONCLUSIONS AND RECOMMENDATIONS

### 1. Conclusions

The conclusions of the investigation are:

1. Solid solutions of the methane-ethane system are not formed for mole fractions of methane less than 0.45 or more than 0.80.
2. Nearly perfect mixtures ( the pure component solidifies out) are formed over this range.
3. The apparatus is well suited for the study of solid-liquid equilibria in low freezing point mixtures. The apparatus is simple and accurate.
4. It is believed that solid solutions are not formed over the entire range of methane-ethane compositions as there was no indication of solid solution behavior.

### 2. Recommendations

The recommendations of the investigation are:

1. The use of the type of apparatus outlined previously is recommended for study of low temperature and pressure solid-liquid equilibria.
2. If very high purity methane or ethane is desired, it is recommended that the possibility of employing fractional crystallization be studied.

## VII. APPENDIX

### 1. Supplementary Details

#### A. Description of Apparatus and Materials.

The storage vessel employed was a used oxygen cylinder having a volume of approximately 35 liters. The equilibrium and precondensing flasks each had a volume of 500 cc. They were made of pyrex glass.

The valves employed were pinchcocks fastened on to sections of rubber tubing. They were found to work well and did not leak.

The mercury for the manometers was triple distilled.

The liquid nitrogen used was obtained from the cryogenic laboratories ( Bld. 41) and was very pure. Approximately fifty liters were consumed during the investigation.

The methane and ethane gases were purchased from the Mathieson Chemical Company.

The shaker employed derived its agitation from the motor on an air compressor. The motor was suspended on a pivoting joint and held in place by a rubber belt. By tying a piece of rubber tubing around the wheel that the belt passed over, it was possible to agitate the motor on the pivot joint. The shaking device had its base on the motor.

The potentiometer used was a Rubicon instrument sensitive to 0.001 millivolt.

The thermocouple was placed about one half centimeter from the bottom of the equilibrium flask.

VII. APPENDIX (Cont)

B. Discussion of Procedure

It was originally planned to plot temperature versus time curves for the methane-ethane mixtures instead of observing the contents of the equilibrium flask directly in order to determine the freezing point. A temperature versus time curve would theoretically have a break in the rate of cooling when the freezing point of the mixture was reached.

In this investigation it was found that no such break occurred for mixtures of methane and ethane. The most probable reason for failure of this method is associated with the impurities in the methane and ethane starting materials. Temperature versus time curves of pure methane and ethane indicated breaks in the rate of cooling but these were small and not sharply defined (indicating impurities because, for a pure component the temperature remains constant until the entire mass is solidified). Therefore, unless very pure starting materials are used it is not recommended that temperature versus time plots be employed to study solid-liquid equilibrium at low temperatures when visual methods can be better applied.

C. Theoretical Derivation of Equation (1). (theoretical lines)

When a solid and liquid are in equilibrium. (7)

$$\bar{F}_{1L} = \bar{F}_{1S} \quad (2)$$

But for any material the change in free energy,  $dF$  is:

$$d\bar{F}_{1L} = \bar{V}_{1L} dP - \bar{S}_{1L} dT \quad (3)$$

$$d\bar{F}_{1S} = \bar{V}_{1S} dP - \bar{S}_{1S} dT \quad (4)$$

combining (3) and (4), gives:

$$d\Delta\bar{F} = d(\bar{F}_{1L} - \bar{F}_{1S}) = (\bar{V}_{1L} - \bar{V}_{1S}) dP - (\bar{S}_{1L} - \bar{S}_{1S}) dT \quad (5)$$

neglecting the pressure change during freezing for our system gives:

$$d\Delta\bar{F} = d(\bar{F}_{1L} - \bar{F}_{1S}) = -(\bar{S}_{1L} - \bar{S}_{1S}) dT \quad (6)$$

now the free energy of any component in solution is given by:

$$\bar{F}_{1L} = \bar{F}_{1L}^{\circ} + RT \ln a_{1L} \quad (7)$$

$$\bar{F}_{1S} = \bar{F}_{1S}^{\circ} + RT \ln a_{1S} \quad (8)$$

if the pure component separates out upon solidification the activity,  $a_i$  is one, or:

$$\ln a_{1S} = 0 \quad (9)$$

reducing equation (7) to:

$$\bar{F}_{1L} = \bar{F}_{1L}^{\circ}$$

letting the reference state free energy equal zero gives:

$$\bar{F}_{1L} = RT \ln a_{1L} \quad (10)$$

$$\bar{F}_{1S} = 0 \quad (11)$$

substituting these values into equation (6) yields:

$$dRT \ln a_{1L} = (\bar{S}_{1S} - \bar{S}_{1L}) dT \quad (12)$$

over a finite temperature range:

$$\Delta RT \ln a_{1L} = (\bar{S}_{1S} - \bar{S}_{1L}) \Delta T \quad (13)$$



taking the lower limit as the freezing point of pure component gives: ( $a_{iL} = 1$ )

$$RT \ln a_{iL} = (S_{iL} - S_{iL}) (T_f - T_{fp}) \quad (14)$$

Now:

$$(S_{iL} - S_{iL}) = \Delta S_{fi} \quad (15)$$

and:

$$S_{fi} = \frac{\Delta H_{fi}}{T_f} \quad (16)$$

substituting (15) and (16) into (14) and rearranging gives:

$$\ln a_i = \frac{\Delta H_{fi}}{RT_f} (T_f - T_{fp}) \quad (17)$$

but:

$$\Delta H_{fi} = \Delta H_{fi}^{\circ} + (C_{pLi} - C_{pIs}) (T_{fp} - T_f) \quad (18)$$

or:

$$\ln a_i = \frac{\Delta H_{fi}^{\circ} + (C_{pLi} - C_{pIs}) (T_{fp} - T_f)}{RT_f} (T_{fp} - T_f) \quad (19)$$

Data on the heat capacities of methane and ethane solid and liquid at low temperatures could not be obtained.

However, an equation was obtained from the literature (6).

This equation was used to calculate the activity of methane and ethane in solution :

$$-\ln N_i = A(T_{fp} - T_f) [1 + B(T_{fp} - T_f) \dots 1] \quad (20)$$

where:

$$A = \frac{\Delta H_{ifp}}{RT_{fp}} \quad (21)$$

$$B = \frac{1}{T_{fp}} - \frac{\Delta C_{pifp}}{2\Delta H_{ifp}} \quad (22)$$

The constants A and B were given as: (6)

1. Methane,  $A = 0.0138$ ,  $B = 0.0057$ .

2. Ethane,  $A = 0.0426$ ,  $B = 0.0095$ .

However, these constants were changed to:

1. Methane,  $A = 0.0142$ ,  $B = 0.0059$ .

2. Ethane,  $A = 0.0432$ ,  $B = 0.0096$ .

The change was brought about by taking the original constants and making them applicable for the freezing point of the pure methane and ethane observed experimentally.

( correction of  $T_f$  )

The  $\Delta H$  of fusion at  $T_{fp}$  of methane and ethane were found to be:

1. Methane,  $\Delta H_{fp} = 0.225$  K.cal./ gram mole

2. Ethane,  $\Delta H_{fp} = 0.683$  K.cal./ gram mole

also: ( freezing points used to calculate constants A and B)

1.  $T_{fp}$  ethane =  $89.89^\circ$  K. or  $-183.27^\circ$  C.

2.  $T_{fp}$  methane =  $90.68^\circ$  K. or  $-182.48^\circ$  C.

The theoretical lines were plotted from equation (19) by assuming a  $\Delta T$  and calculating the corresponding  $N_1$ .

## VII. APPENDIX (Cont.)

### 2. Summary of Data and Calculated Values

The original data obtained were in the form of pressures (in cm. Hg.) in the storage cylinder, temperature (in °C.) of the storage cylinder, and potentiometer readings (in millivolts). Temperatures are read to  $\pm 0.05^\circ\text{C}$ ., pressures to  $\pm 5$  mm. Hg., and potentials are read to the values given on the following table.

Table 1.

Pure Methane

Run 1.

Initial Pressure mm.	Final Pressure mm.	Initial Temperature °C.	Final Temperature °C.	Potentiometer Reading millivolts
7.96	66.31	28.20	28.20	$5.307 \pm 0.005$
Pressures of pure ethane mixed with above methane.				
3.00	10.71	28.86	28.86	$5.420 \pm 0.005$
3.00	13.23	28.86	29.40	$5.455 \pm 0.005$
3.00	15.51	28.86	29.68	$5.480 \pm 0.005$
3.00	16.84	28.86	29.50	5.498 no solid.

Run 2.

Pure Ethane

16.97	64.33	27.93	27.30	$5.309 \pm 0.003$
Pressures of pure methane mixed with Run 2. (above) ethane.				
21.59	24.60	26.10	26.10	$5.343 \pm 0.002$
21.59	26.79	26.10	26.00	$5.360 \pm 0.002$
21.59	30.52	26.10	25.78	$5.387 \pm 0.002$
21.59	34.25	26.10	25.80	$5.400 \pm 0.003$
21.59	36.73	26.10	25.75	$5.413 \pm 0.002$
21.59	40.16	26.10	25.10	$5.437 \pm 0.005$
21.59	44.42	26.10	26.23	$5.450 \pm 0.002$
21.59	48.60	26.10	26.50	$5.465 \pm 0.005$
21.59	52.37	26.10	27.00	$5.475 \pm 0.002$

(table continued on next page)

Table 1. (Cont.)

Initial Pressure mm.	Final Pressure mm.	Initial Temperature °C.	Final Temperature °C.	Potentiometer Reading millivolts
21.59	55.08	26.10	27.20	5.480 ± 0.002
21.59	58.65	26.10	27.50	5.488 ± 0.002
21.59	60.63	26.10	27.90	5.496 ± 0.002
21.59	61.63	26.10	28.20	5.498 ± 0.002
21.59	63.03	26.10	24.40	5.500 no solid

Liquid nitrogen reference potential = 5.505

From the above data ( table 1.) the following quantities were calculated:

1. Values of the pressure corrected for temperature differences.
2. Values of,

$$\frac{P_{\text{CH}_4} T_{\text{C}_2\text{H}_6}}{P_{\text{C}_2\text{H}_6} T_{\text{CH}_4}} = \frac{N_{\text{CH}_4}}{N_{\text{C}_2\text{H}_6}} \quad \text{assuming perfect gas laws} \quad (23)$$

3. Values of temperature from graph four.
4. Values of mole fraction methane from values of  $\frac{N_{\text{CH}_4}}{N_{\text{C}_2\text{H}_6}}$ .
5. Values of  $(T_{\text{fp}} - T_f)$ . (or  $\Delta T$ )

The perfect gas laws were assumed during the course of the investigation. It is an excellent assumption at the pressures and temperatures used, and simplifies the calculations greatly. The pressure was corrected to that pressure that would be exerted at a reference temperature, or from the perfect gas law:

$$\frac{P_{\text{corrected}}}{P_{\text{observed}}} = \frac{T_{\text{reference}}}{T_{\text{observed}}} \quad (\text{since } N, R, \text{ and } V \text{ are constant}) \quad (24)$$

The following values were obtained.

Table 2.

$\Delta P$ corrected	$\frac{N_{CH_4}}{N_{CH_4} + N_{C_2H_6}}$	Mole Fraction methane	Temperature °Kelvin	$\Delta T$ °K
Pure methane		Run 1		
58.35	-	1.0000	301.20	0
Pure ethane mixed with above methane				
7.71	0.132	0.883	301.86	6.9
10.20	0.174	0.852	301.86	9.0
12.47	0.213	0.824	301.86	10.6
13.80	0.236	0.809	301.86	11.7
Pure ethane		Run 2		
47.49	--	1.000	300.92	0
Pure methane mixed with above ethane (run 2).				
3.01	0.064	0.060	299.10	2.0
5.21	0.110	0.099	299.10	3.0
8.92	0.189	0.159	299.10	4.6
12.69	0.269	0.212	299.10	5.4
15.18	0.322	0.243	299.10	7.3
18.70	0.396	0.284	299.10	7.7
22.81	0.483	0.326	299.10	8.6
26.99	0.572	0.364	299.10	9.5
30.62	0.649	0.393	299.10	10.1
33.29	0.705	0.413	299.10	10.4
36.79	0.779	0.438	299.10	10.9
38.67	0.819	0.450	299.10	11.4
39.61	0.839	0.456	299.10	11.5
41.80	0.886	0.470	299.10	11.6

Calculated  $\Delta T$ 's are good to  $\pm 0.2^\circ C$ .

Calculated Pressure changes ( $\Delta P$ ) are good to  $\pm 0.10$  mm. Hg.

Calculated mole fractions methane are good to  $\pm 0.01$ .

## VII. APPENDIX (Cont.)

### 3. Nomenclature

$F_{1L}$	Free energy of component one in the liquid phase.
$F_{1S}$	Free energy of component one in the solid phase.
$V_{1L}$	Specific volume of component one in the liquid phase.
$V_{1S}$	Specific volume of component one in the solid phase.
$S_{1L}$	Entropy of liquid at the freezing point of component one.
$T_{fp}$	Freezing point of pure component.
$T_f$	Freezing point of the mixture under study.
$a_{1L}$	Activity of component one in the liquid phase
$\Delta H_{1fp}$	Heat of fusion of the pure component at the freezing point of the mixture
$C_{p1fp}$	Specific heat of component one at the freezing point of the mixture.
$N_{1L}$	Mole fraction of component one in the liquid phase.

#### 4. Literature Citations

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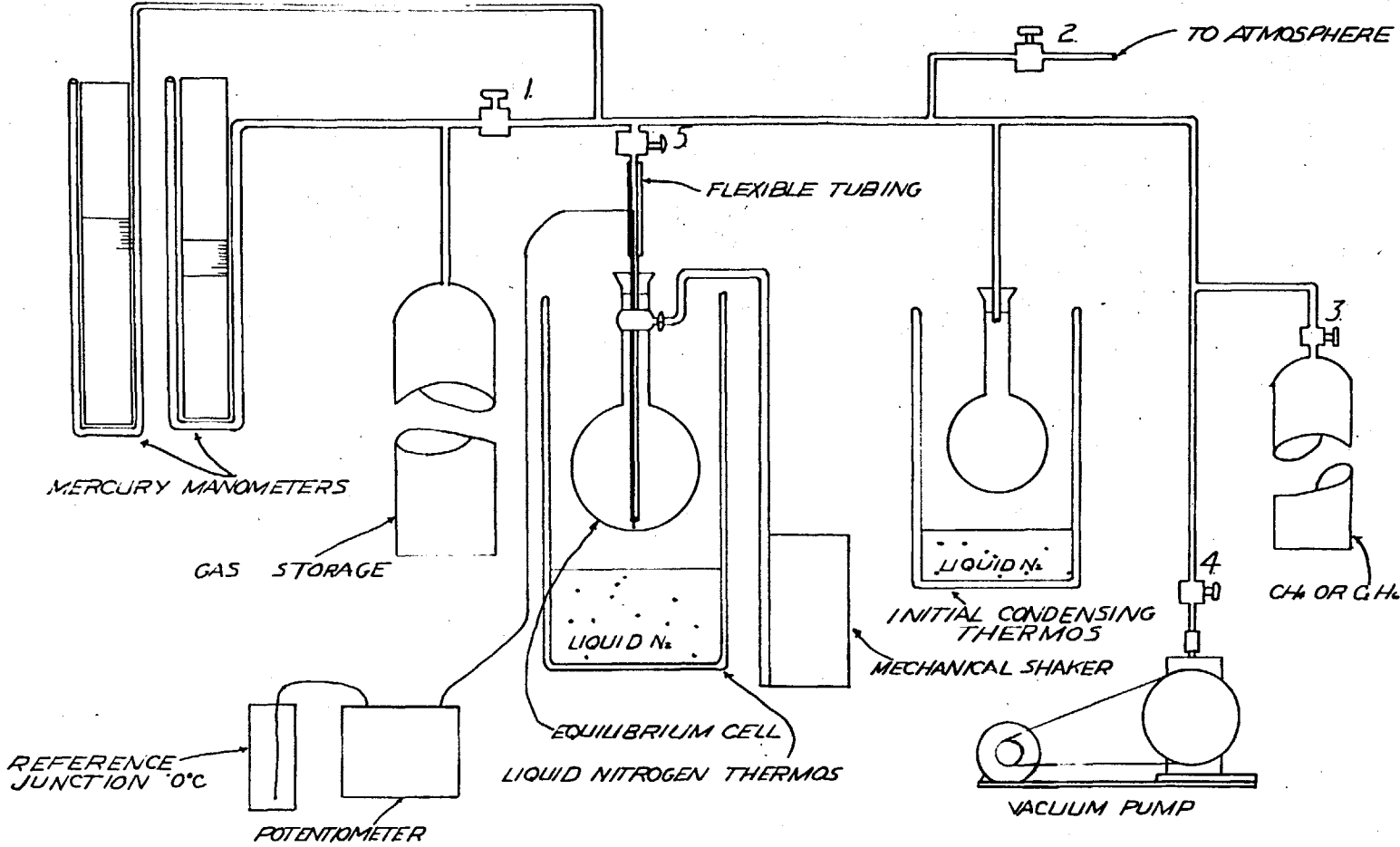
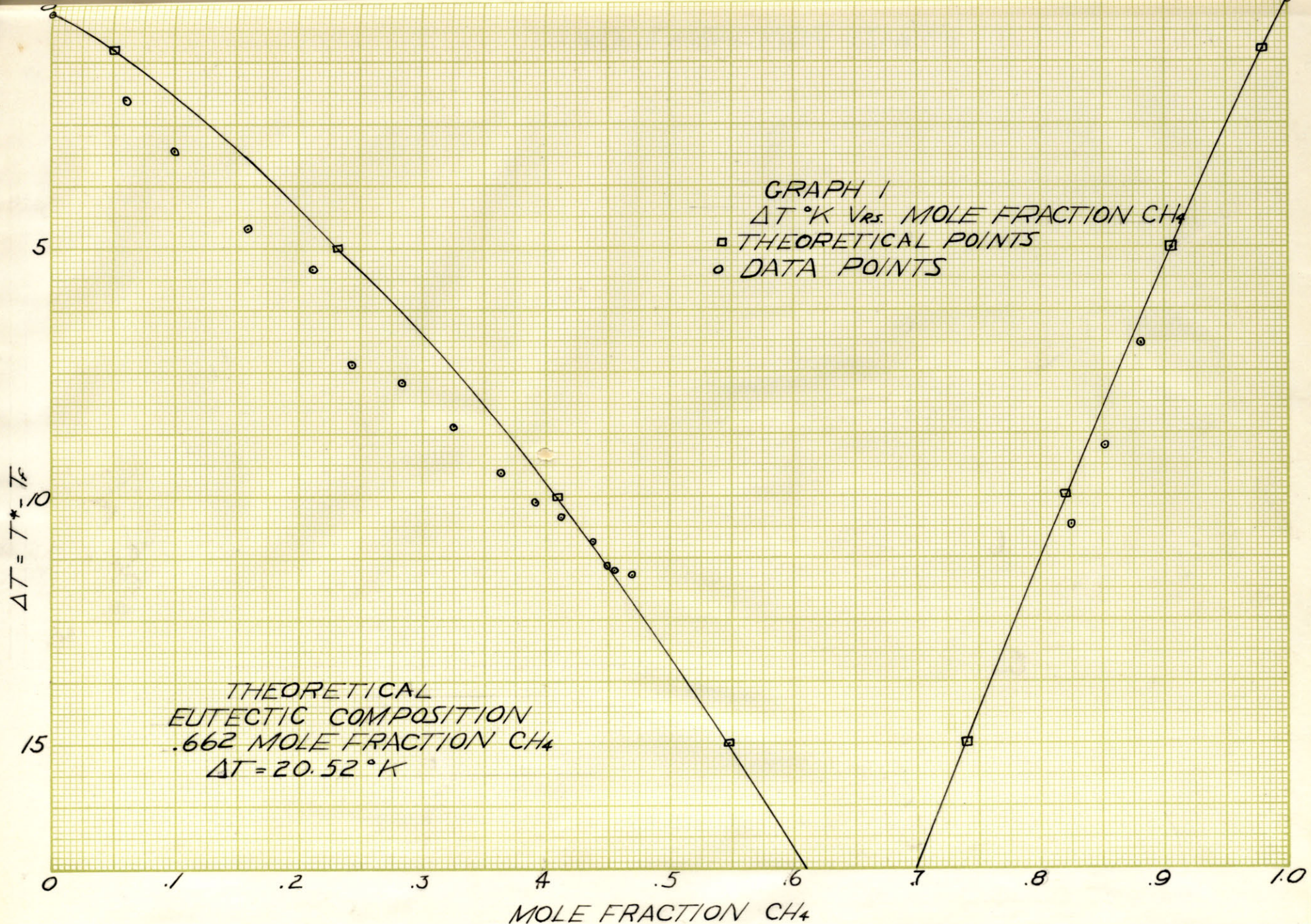
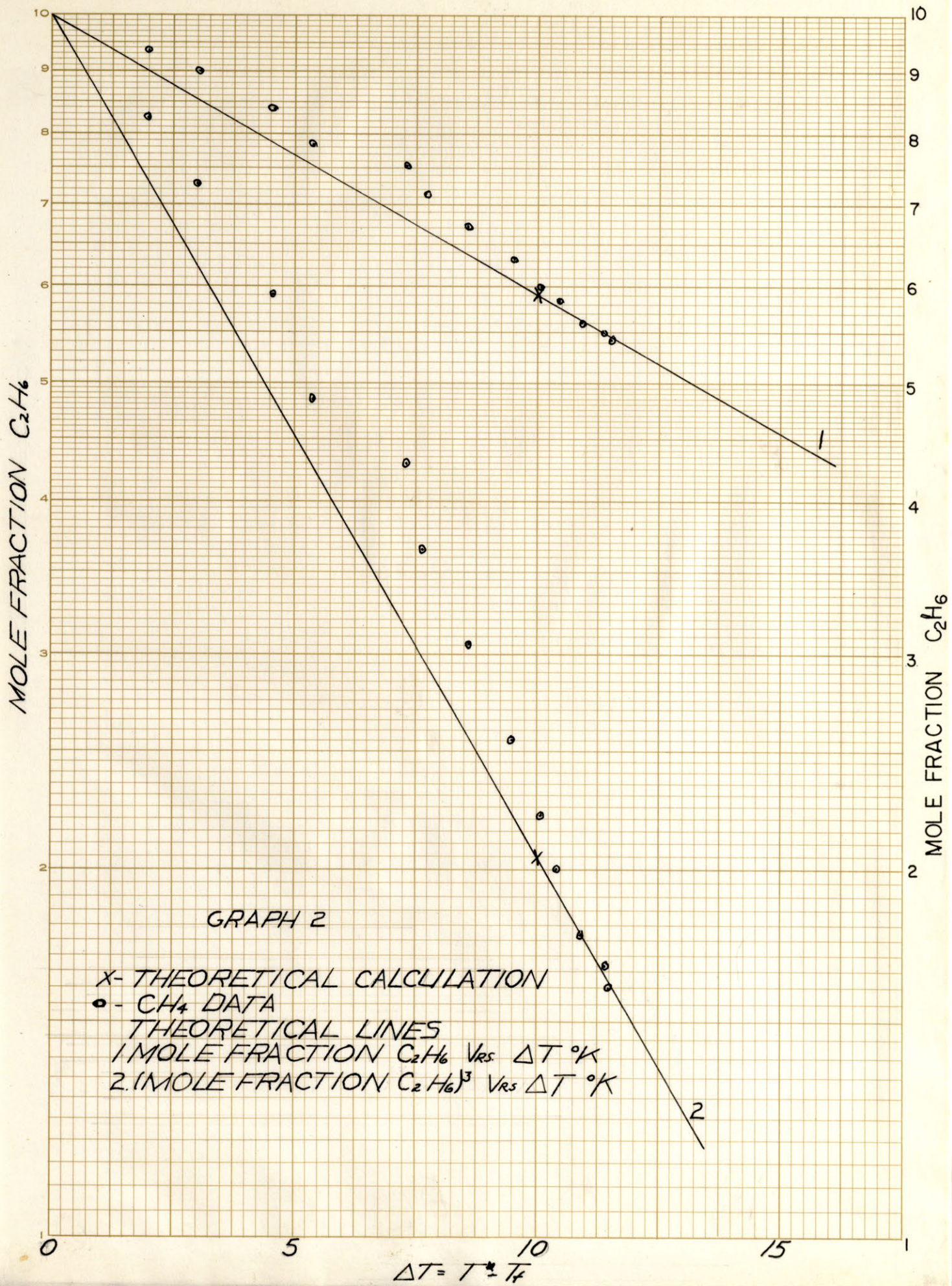


FIGURE 1  
 APPARATUS FOR THE STUDY OF  
 METHANE ETHANE EQUILIBRIA





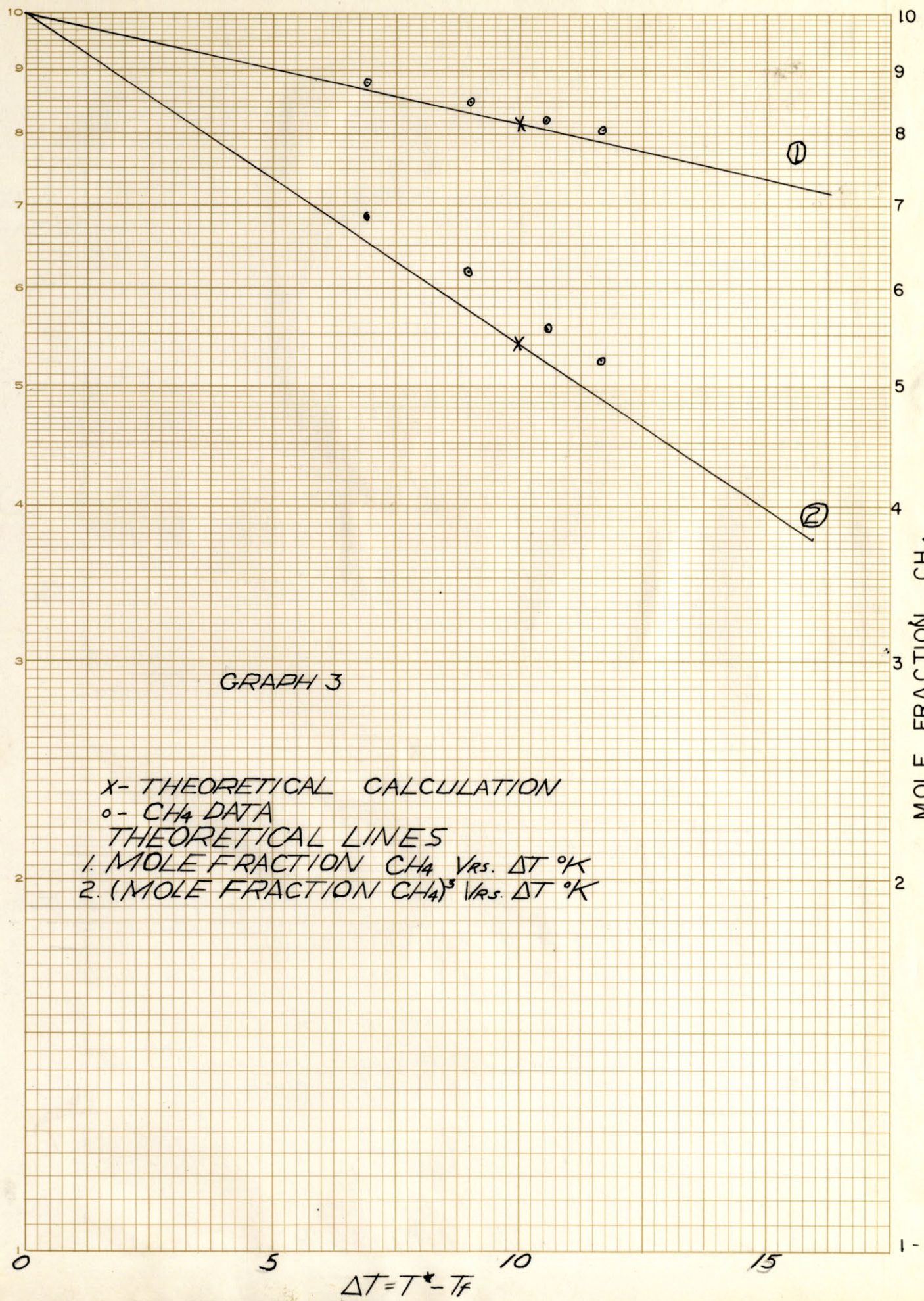






MOLE FRACTION CH<sub>4</sub>

MOLE FRACTION CH<sub>4</sub>



GRAPH 3

X - THEORETICAL CALCULATION  
 o - CH<sub>4</sub> DATA  
 THEORETICAL LINES  
 1. MOLE FRACTION CH<sub>4</sub> VRS.  $\Delta T$  °K  
 2. (MOLE FRACTION CH<sub>4</sub>)<sup>3</sup> VRS.  $\Delta T$  °K



LIQUID N<sub>2</sub>  
0115, -1958

REFERENCE  
JUNCTION °C.

°C

GRAPH 4

-180

-185

-190

-195

-200

5.30

5.35

5.40

5.45

5.50

5.55

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