

The Low Temperature Heat Capacity of Gaseous Ethane

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the Li^+H^- curve reach the same slope should furnish the basis for an estimate of the dissociation energy of the normal state, since the energy difference between states V and N is known precisely from the spectroscopic data. From a rough estimate of the point at which the slope of the state V curve is closest to that of the Coulombic curve, the state N curve should be lifted with respect to its asymptote by about 0.2 ev above Mulliken's estimate of its position. This would make the dissociation energy of normal LiH about 2.3 ev.

According to the present computations, however, the state V curve is flatter at moderately large r values than Mulliken supposed, and must actually cross the Li^+H^- curve, apparently going to $\text{Li}(^2P)+\text{H}$. If Mulliken's value of 0.75 ev for the height of the state V curve above $\text{Li}(^2S)+\text{H}$ is accepted as a reasonable estimate, the crossing point is in the neighborhood of 3.8Å. This shows that the interaction of the Li^+H^- curve with the unperturbed $\text{Li}(^2P)\cdot\text{H}$ curve is much more intense near 5Å than is indicated by Fig. 2 of reference 5, so that state V dissociates quite definitely into $\text{Li}(^2P)+\text{H}$. Aside from this

quantitative change at large r values, the present results give no reason for altering Mulliken's interpretation of the nature of state V . The position of the Coulombic curve seems to make it unavoidable that state V be predominately of Li^+H^- character over a range of moderately large r values before it goes over into $\text{Li}(^2P)+\text{H}$.

These conclusions, unfortunately, do not help to fix a precise value of the dissociation energy of the normal state, a quantity which is particularly interesting because the values proposed for it are considerably below that required by Pauling's additivity rule.⁶ The value of 2.5 ev adopted by Mulliken is still a reasonable one and is compatible with the portion of the potential energy curve which has here been obtained. But the basis on which this value was reached has been made less certain. It may be said, however, that from the rate at which the state V curve beyond its inflection point is bending, a value less than 2.6 ev is more likely than a larger one.

I wish to record my thanks to Professor Mulliken for many valuable discussions.

⁶ Pauling, J. Am. Chem. Soc. **54**, 3570 (1932). This situation is discussed by Mulliken in reference 5.

The Low Temperature Heat Capacity of Gaseous Ethane

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The heat capacity of ethane has been determined at 163° and 143°K by the "hot wire" method and has been found not to level off as suggested earlier by Eucken and Weigert. This speaks against free interval rotation in ethane molecules.

SOME time ago Eucken and Weigert¹ employed the "hot wire" technique, devised by Schleiermacher² and since used repeatedly by others, to measure the heat capacity of ethane down to very low temperatures. The most significant result of this work was the observation that at the lowest temperature studied, *ca.* 140°K, the heat capacity curve of ethane gave indications of leveling off appreciably above the

classical value, $3R$, for the heat capacity due to rotation and translation. Quantum statistical calculations of Teller and Weigert³ showed that this behavior was to be expected if only a small hindrance to free internal rotation of the methyl groups in ethane was postulated. Eucken and Weigert concluded that a restraining potential of *ca.* 300 cal./mole fitted their observations best, meaning that at room temperature the methyl groups in an average ethane molecule are freely rotating.

¹ Eucken and Weigert, Zeits. f. physik. Chemie **B23**, 265 (1933).

² Schleiermacher, Wied. Ann. **26**, 287 (1886).

³ Teller and Weigert, Nachr. Götting. Ges. **218** (1933).

Eyring⁴ treated the problem of internal rotation in ethane by approximate methods of quantum mechanics (taking into consideration interactions of pairs of electrons but neglecting all higher approximations) and likewise concluded that a potential barrier (restraining potential) of about 300 cal./mole exists.

Measurements of the thermal equilibrium between ethane, ethylene and hydrogen at higher temperatures have been available for some time.⁵ When the heat of hydrogenation of ethylene was determined in this laboratory,⁶ it became possible with the help of statistically calculated entropies to examine the internal consistency of the data. This was done by Smith and Vaughan⁷ and more carefully by Teller and Topley,⁸ but all arrived at the same conclusion that the thermochemical and equilibrium data were irreconcilable if the Eucken internal potential was adopted in the calculation of the entropy of ethane. Smith and Vaughan concluded that the statistical entropy calculations were in error due to the assumption of practically free rotation in ethane. Teller and Topley chose, however, to consider the calorimetric value in error. A check from this laboratory⁹ demonstrated the correctness of the published figure of the heat of hydrogenation of ethylene, while Rossini¹⁰ obtained a practically identical value from heats of combustion. Thus no doubt can remain that the calorimetric value of the heat of reaction is correct.

It is, of course, possible that the equilibrium measurements are misleading, but the correction required to account for the above discrepancy amounts to a factor of 2 to 3 in the equilibrium constant. Although methane and therefore some olefins other than ethylene are formed to some extent as by-products of the dehydrogenation of ethane¹¹ (cf. the paper by Pease⁵) the excellent

agreement of four available sets of equilibrium measurements indicates that an error of such magnitude is highly improbable. It is to be noted that some of the published measurements have been performed on the homogeneous reaction, others on the heterogeneous process which was accelerated by several catalysts; together they cover a wide temperature and pressure range. One is led, therefore, to the conclusion that the equilibrium measurements are not in error.

Indeed, Howard,¹² in his analysis of the normal coordinate problem of ethane-like molecules, arrived at the conclusion that the rotational structure of the infrared bands of ethane can be explained only if a restraining potential of *at least* 2000 cal. exists in this molecule.

Important additional evidence against the existence of nearly unhindered rotation in ethane was obtained by Witt and Kemp¹³ in their study of the heat capacity of solid and liquid ethane at low temperatures. Kemp and Pitzer¹⁴ pointed out that the third law entropy of ethane derived from these measurements is considerably lower than that calculated statistically for the model with the Eucken restraining potential. It is true, of course, that in several well-known instances the observed entropy has been found too low because of imperfect reversibility of the heat capacity measurements at very low temperatures, either within the range covered in the calorimeter or in the extrapolation to the absolute zero; but in the case of ethane no reasons have been advanced to justify the assumption of such errors. Statistical calculations of Kemp and Pitzer reproduce the value of Witt and Kemp, if *ca.* 3100 cal. is assumed for the internal restraining potential in ethane; then the thermal equilibrium measurements become consistent with the measured heat of hydrogenation and the heat capacity of gaseous ethane at higher temperatures^{8, 14} falls on the statistical heat capacity curve.

Therefore, little doubt can be left that ethane does not possess the free rotation postulated by Eucken. The present contribution advances the evidence further by showing that the heat

⁴ Eyring, J. Am. Chem. Soc. **54**, 3191 (1932).

⁵ (a) Pease and Durgan, J. Am. Chem. Soc. **50**, 2715 (1928). (b) Frey and Huppke, Ind. Eng. Chem. **25**, 54 (1933). (c) Travers and Pearce, J. Soc. Chem. Ind. **53**, 322T (1934). (d) Videnski and Vinikova, J. Gen. Chem. Moscow **4**, 120 (1934).

⁶ Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan, J. Am. Chem. Soc. **57**, 65 (1935).

⁷ Smith and Vaughan, J. Chem. Phys. **3**, 341 (1935).

⁸ Teller and Topley, J. Chem. Soc. 876 (1935).

⁹ Kistiakowsky and co-workers, J. Am. Chem. Soc. **58**, 137 (1936).

¹⁰ Rossini, Nat. Bur. Stand. J. Research **17**, 629 (1936).

¹¹ Private communication from Dr. Louis S. Kassel.

¹² J. B. Howard, J. Chem. Phys. **5**, 451 (1937).

¹³ Witt and Kemp, J. Am. Chem. Soc. **59**, 273 (1937).

¹⁴ Kemp and Pitzer, J. Am. Chem. Soc. **59**, 276 (1937).

capacity curve of gaseous ethane at low temperatures does not level off as the data of Eucken and Weigert suggested.

No method exists at present which is capable of determining directly the heat capacity of gases at low pressures. Despite its several objectionable inherent weaknesses, the "hot wire" method was used in the present work because of the low vapor pressure of ethane at the temperatures of interest.

According to Knudsen,¹⁵ the heat loss per unit area from a thin wire suspended in a cylindrical vessel filled with a gas at such a low pressure that the mean free path of gas molecules is large compared to the diameter of the vessel, is given by:

$$\Delta Q = \frac{1}{(6\pi)^{\frac{1}{2}}} \cdot n \cdot \bar{w} \cdot \alpha [2R + (C_v - 3/2R)] \cdot \Delta T, \quad (1)$$

where n is the number of molecules per cc, \bar{w} is the mean molecular velocity, C_v is the heat capacity of the gas, ΔT is the temperature difference between the wire and the walls of the vessel, while α is the accommodation coefficient of the gas on the surface of the wire. This coefficient must be introduced because, according to Knudsen, the gas molecules do not reach thermal equilibrium with a solid surface upon their first collision with it, so that the observed heat conductance is smaller than that calculated without the accommodation coefficient.

Numerous investigations, which we shall not discuss, have shown that the accommodation coefficient depends on the nature of the solid surface and on the nature of the gas, and also on the temperature. It ranges from unity to less than 0.1. A survey of this work indicates that the accommodation coefficient usually decreases with increasing temperature, but at high temperatures begins to rise again, although exceptions to this behavior have been observed.

Because of the uncertainty of the accommodation coefficients, measurement of heat conductance by the gas gives only a lower limit of the heat capacity, and does not in general reproduce correctly even its temperature dependence. Eucken and Weigert's procedure in eliminating the objectionable accommodation coefficient

consisted in measuring first the heat conductances of two gases (argon and ethane) at temperatures so high that reliable data on the heat capacities of both could be secured by other methods. By forming the ratio of Eqs. (1) for the two gases and substituting their heat capacities, a ratio of accommodation coefficients was calculated which, experimentally, showed a tendency to approach unity with decreasing temperature. For the purposes of extrapolation to low temperatures, at which the heat capacity of only one gas was known, it was assumed that the ratio did actually approach unity. The heat capacity of the other gas was then readily calculated.

EXPERIMENTAL DETAILS

The general principle of the method of Eucken and Weigert has been adopted for the present experiments, but some modifications were introduced. Since the accommodation coefficient depends rather decisively on the structure of the solid surface, an apparatus was constructed which contained four different wires, with the hope that the average of measurements on all would give more reliable results. Three of the wires selected were the usual blank drawn platinum wires: the first as supplied by the manufacturer (0.02 mm diameter); the second wire was electrolytically coated with an active deposit of platinum black and the third was electrolytically coated with a coarse porous deposit of nickel, and later oxidized in air by heating. The fourth wire was a blank drawn nickel wire oxidized in air. Thus, of the four surfaces two were metallic, one relatively smooth, the other decidedly irregular; two were coated with oxide, one smooth and the other rough.

The thin wires (H , Fig. 1), *ca.* 20 cm in length, were mounted co-axially in cylindrical holes (1 mm diameter) drilled in brass rods *ca.* 10 mm in diameter (R). One end of the wire was soldered to the rod, the other passed through a narrow hole in a thin mica plate (m) mounted at the end of the rod and was held under gentle tension by an insulated tungsten spring (s). Very near the mica plate two heavier wires (W) were fused to the thin wire. This entire unit was sealed in a glass tube (G) of a diameter somewhat

¹⁵ M. Knudsen, *Ann. d. Physik* **34**, 593 (1911).

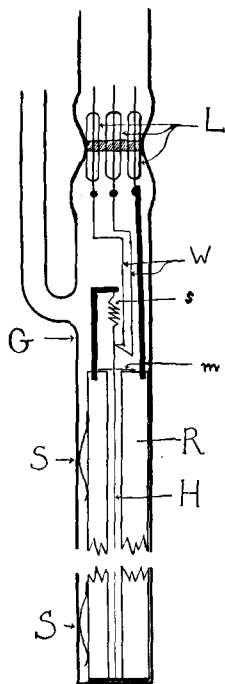


FIG. 1.

larger than that of the brass rods. The latter were pressed against the glass walls by suitable springs (*S*). A wire from the brass rod and the two fused to the end of the heater wire were connected with the outside by means of tungsten-in-glass seals (*L*). Direct measurements showed that the temperature of the brass rods was less than 0.02°C above that of the outside of the glass tube when the heater wire was heated as in experiments to be described. This agrees with calculations which consider the diameter of the wire, of the brass rod and the heat conductance by the gas.

The glass tubes containing the wires were joined to a thermostated 5-liter flask, which communicated with a thermostated system of gas pipettes for admitting accurately measured small amounts of various gases into the system. The flask was also connected through a large stopcock with a fast pumping system. Apiezon stopcock grease was used throughout. A Pirani gauge, constructed as the other units, was attached to the system and kept in an ice bath.

The "hot wires" were placed in a large Dewar cylinder provided with a stirrer, a small electric heater and liquid-filled temperature regulator.

The regulator, as well as the Dewar vessel, was filled with the light fraction of the "gas-machine" gasoline, b.p. below 40°C . The cooling agent (solid carbon dioxide or liquid air) was contained in a double-walled glass cylinder mounted within the larger Dewar vessel. The interspace of the cooling vessel was permanently connected to a mercury vapor pump, the fore-vacuum side of which was closed from the oil pump, during the experiments. A by-pass from the fore-vacuum side of the pump to the interspace led through a fine needle valve, provided with syphon bellows instead of packing. The valve was driven by reversible Telechron motor, the two coils of which were attached to the two poles of a relay operating also the heating element in the large Dewar vessel.

This arrangement operates in such a way that when the heater is on, the Telechron motor turns in a direction which slowly closes the valve so that the mercury pump reduces the gas pressure in the interspace between the cooling agent and the thermostat liquid. The heat conductance between them therefore gradually decreases. The reverse process is taking place with the heater off. When a perfect balance of heat flow has been obtained, the valve executes small symmetric oscillations around a fixed position, since the heater is half of the time on and half of the time off. But when the heat balance has been disturbed (as for instance by a loss of the cooling agent) and the heater is, let us say, most of the time in the off position, the valve begins to execute unsymmetric oscillations, the trend being on the average to open it more, thus admit more gas to the interspace and thereby increase the heat conductance. This process continues until the heat balance has been re-established and the heater is again operating in the most favorable manner, being half of the time off and half on. Thus it is possible to delay refilling the cooling agent for longer times and yet have the cryostat operate at a constant temperature without measurable drifts. Regular variations were found to amount to at most 0.03° , but improvements in the regulator design could easily reduce this further.

The temperatures were measured with a 5-junction copper-constantan thermel, a correction to the I.C.T. thermal e.m.f. data being

determined at the oxygen and solid carbon dioxide points and at the transition temperature of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$.

The electrical system consisted of a Mueller type L. & N. bridge operated from a large 12-volt storage battery through variable resistances; because of the three wire connections only the resistance of the thin portions of the "hot wire," within the 1 mm holes, was measured. In series with the wires was a standard resistance across a type K, L. & N. potentiometer, used also to measure the e.m.f. of the thermel.

The procedure during a typical run consisted in evacuating the system to better than 10^{-5} mm Hg, while the cryostat was being cooled to the desired temperature. The resistance of the wires at the cryostat temperature was determined by extrapolating their resistance to zero heating current. Thereupon the current was increased until the temperature of the wires was 20° higher. The current was determined by measuring the potential drop across the standard resistance and the square of it gave a relative measure of the heat losses by radiation and by end conduction. Then the system was flushed two or three times with the gas and filled to a fixed pressure, and the current needed to keep the wire at the same temperature was determined. Most of the measurements were made with the same pressure of

3.2×10^{-2} mm, but a few measurements made at different pressures gave the same values of the accommodation coefficients. The difference of the square of the current with and without the gas gave a relative measure of the heat conducted by the gas. The system was evacuated and the entire procedure repeated with another gas, care being taken that exactly the same amount of gas was admitted and that the temperature of the wire remained unchanged.

THE RESULTS AND DISCUSSION

Heat conductance by argon, methane, ethylene, ethane, propylene, propane, butene-2 (*trans*) and butene-2 (*cis*) has been determined. For the four last gases no reliable heat capacity data are available as yet. Pending their determination a discussion of their heat conductance will be postponed.

Table I illustrates the method of calculating the results from the observed values of the potential across the standard resistance. Since the temperature, and therefore the resistance of the wires, remains constant during all measurements, and the gases are at the same concentration, ΔT and n drop out of the equation (1) when the ratio of two heat conductances is formed:

$$\frac{\Delta Q''}{\Delta Q'} = \frac{(M')^{\frac{1}{2}} [2R + (C_v'' - 3/2R)] \alpha''}{(M'')^{\frac{1}{2}} [2R + (C_v' - 3/2R)] \alpha'} \quad (2)$$

TABLE I. *Methane and ethylene. Temperature of the bath, 273.10°K. Temperature of the wires, 293.10°K.*

	(Pt) I	(Ni-Ni ₂ O ₃) II	(Pt-Pt bl.) III	(Pt-Ni ₂ O ₃) IV
Resistance at 293° in ohms	37.980	30.630	37.125	33.930
Vacuum e^*	0.0418	0.0871	0.0907	0.1120
Methane E''^*	0.1513	0.1916	0.1857	0.2189
Ethylene E'^*	0.1503	0.1888	0.1812	0.2146
$\frac{\Delta Q''}{\Delta Q'} = \frac{E''^2 - e^2}{E'^2 - e^2}$	1.014	1.037	1.067	1.056
Experiment repeated two days later				
e^*	0.0423	0.0876	0.0913	0.1123
E''^*	0.1513	0.1918	0.1857	0.2190
E'^*	0.1505	0.1891	0.1814	0.2149
$\frac{\Delta Q''}{\Delta Q'} = \frac{E''^2 - e^2}{E'^2 - e^2}$	1.013	1.037	1.064	1.053
Average	1.013	1.037	1.065	1.055
C_v' ethylene (283.1)	8.02			
C_v'' methane (283.1)	6.44			
from Eq. (2) α''/α' (283.1)	0.929	0.950	0.977	0.968

* Potential across standard resistance.

To calculate the ratio of accommodation coefficients from (2) the heat capacities of the two gases must be known. The following values have been used:

For argon the value $\frac{3}{2}R$ was used throughout.

The heat capacity of methane was taken from Eucken and Bertram¹⁶ and for the lowest temperatures was calculated statistically.

For ethylene, the values given by Eucken and Parts,¹⁷ were used. For the lower temperatures a statistical calculation using the frequencies given by Bonner¹⁸ was made, assuming classical rotation and a rigid rotator-harmonic oscillator model.

The heat capacity of ethane from 303 to 193°K was taken from Eucken and Parts; graphical interpolation was used and the figures reduced to ideal gas state.

The accommodation coefficient ratios, calculated in the manner shown in Table I, have been collected in Table II. Each of the values there given is the average of two independent determinations, the deviations from the mean being never larger than 0.4 percent but usually considerably less.

Several rather instructive facts emerge upon the study of Table II. Eucken and Bertram¹⁶ contend that the nickel-nickel oxide wire is exceptionally favorable in giving accommodation coefficient ratios near unity. The table shows that the differences between the several surfaces used are extremely small and that, if anything, the platinum black surface is the best one from this point of view. The absolute values of the accommodation coefficient ratios are lower throughout than those of Eucken. This may be due to a differently conditioned surface but perhaps also to the circumstance that Eucken's method does not completely eliminate the radiation correction, as may be done when the wire is maintained throughout at the same temperature.

There appears to be no advantage in using argon as done by Eucken for the reference gas since the accommodation coefficient ratios in

TABLE II. Ratios of the accommodation coefficients.

	T°K	I (Pt)	II (Ni-Ni ₂ O)	III (Pt-Pt bl.)	IV (Pt-Ni ₂ O)
CH ₄ /A	283	0.845	0.848	0.900	0.880
	243	0.876	0.895	0.921	0.910
	223	0.888	0.905	0.920	0.915
	195	0.905	0.919	0.931	0.925
CH ₄ /C ₂ H ₄	283	0.929	0.950	0.977	0.968
	243	0.932	0.955	0.982	0.972
	223	0.930	0.953	0.975	0.970
	195	0.936	0.952	0.977	0.972
	163	0.931	—*	—*	0.957
	143	0.950	—*	—*	0.989
C ₂ H ₆ /C ₂ H ₄	303	1.011	1.030	1.009	1.016
	283	1.005	1.016	1.002	1.010
	243	1.002	1.013	1.002	1.005
	223	1.013	1.012	1.001	1.002
	193	1.005	1.009	1.005	1.007

* Units broken.

this case show a particularly pronounced temperature variation.

The ratio of the accommodation coefficients of methane to ethylene, which is essentially independent of temperature in the range from 283 to 163°K, shows a sudden rise at 143°K. A probable explanation of this peculiar behavior was discovered through measurements of the pressure of gas admitted to the system with the "hot wire" vessels immersed in liquid oxygen. At higher temperatures the pressure of each gas was found to be the same when admitted to the system from the same pipette at a fixed pressure, whereas at the temperature of liquid oxygen it was found that the pressure of methane was appreciably higher than that of the other gases. (See Table III.)

It is evident, therefore, that ethylene and ethane are adsorbed in greater amounts on the cold parts of the system than is methane. Probably this polymolecular film adsorption¹⁹ starts at 143°K, producing a slightly lower pressure of ethylene in the system and thus simulating an abnormally high accommodation coefficient of methane.

TABLE III. Pressures at liquid oxygen temperature.

	METHANE	ETHANE	ETHYLENE
mm Hg	1.25×10^{-2}	0.95×10^{-2}	0.95×10^{-2}

¹⁶ Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 363 (1936).

¹⁷ Eucken and Parts, Zeits. f. physik. Chemie **B20**, 184 (1933).

¹⁸ Bonner, J. Am. Chem. Soc. **58**, 34 (1936).

¹⁹ Because of the large volume of the system a unimolecular film adsorption in the "hot wire" tubes does not affect the gas pressure significantly.

Of great importance for the following is that even at liquid oxygen temperature the residual pressures of ethane and of ethylene are the same; hence, these two gases are adsorbed in equal amounts; the same undoubtedly is true at the temperature of 143°K, when the total adsorption is still quite small.

As Table II shows, the accommodation coefficient ratios of ethane to ethylene are very near unity at all temperatures and on all wires. A small temperature trend does exist, which in all instances seems to bring the ratios nearer unity with decreasing temperature. But in any case an extrapolation over some 50° to 143°K should introduce no significant uncertainties. Table IV shows the selected figures of the ratios of the accommodation coefficients, as well as the heat capacities of ethane deduced therefrom.

The heat capacity of ethane, as determined here and as given by Eucken and Weigert, has been plotted in Fig. 2. The new data show no evidence of the leveling off of the C_v curve above 7 cal./mole as was suggested by the lowest point of the Eucken and Weigert measurements. Instead, a steady decrease is observed, the points falling on the curve calculated by Dr. Pitzer for

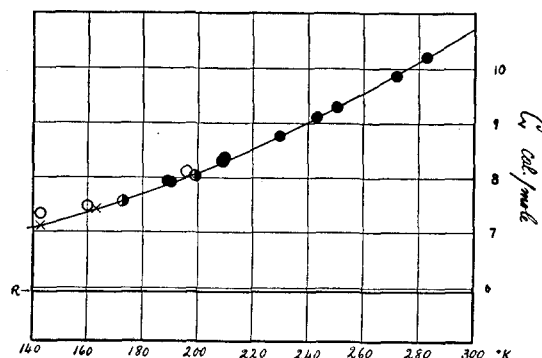


FIG. 2. Dark circles, Eucken and Parts; light circles, Eucken and Weigert; half-darkened circles, Eucken and Bertram; cross, this work; line, theoretical curve of Pitzer, $V_0 = 3100$ cal.

an internal restricting potential of 3100 cal. with the unknown vibrational frequency of ethane being taken as 1100 cm^{-1} . This selection agrees well with the calculation of Howard¹² (1000 cm^{-1}) based on the normal coordinate treatment of ethane. We are indebted to Dr. Pitzer for the permission to use the curve.

The new data, contributing to the evidence discussed in the beginning of the paper, eliminate the last doubts concerning the existence of a large internal restricting potential in ethane, but they do not make its origin more understandable. Dr. Howard, upon an examination of the quantum-mechanical problem of ethane, informs us that calculations which take into account interactions of pairs of electrons, by the usual approximation methods, lead to only small restricting potentials of the same order of magnitude as deduced by Eyring.⁴ The restriction of free rotation around the carbon-carbon single bonds belongs, evidently, to those quantum mechanical problems for which a more refined treatment is needed, than usually given, to obtain an even semi-quantitative agreement with experimental data.

TABLE IV.

$\frac{T_{\text{therm.}} + T_{\text{wire}}}{2}$		I	II	III	IV
193°K	α/α meas. C_v ethylene C_v ethane	1.005 6.46 8.02	1.009	1.005	1.007
163°K	α/α extrapolated C_v ethylene C_v ethane, calc. Average	1.007 6.15 7.40	1.005 7.45 7.43	1.002 7.43	1.001 7.46
143°K	α/α extrapolated C_v ethylene C_v ethane, calc. Average	1.003 6.05 7.11	—* 7.10	1.001 7.09	1.000 7.10

* This unit was broken during this run.