

The Exchange of Energy Between Organic Molecules and Solid Surfaces Part I. Accommodation Coefficients and Specific Heats of Hydrocarbon Molecules

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The Exchange of Energy Between Organic Molecules and Solid Surfaces

Part I. Accommodation Coefficients and Specific Heats of Hydrocarbon Molecules*

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A molecular beam method primarily devised for the investigation of heterogeneous thermal decomposition of hydrocarbon-molecules (to be published later) was used to determine the accommodation coefficients of various hydrocarbon molecules at 20°C on an ordinarily clean nickel surface at 140°C and at pressures in the region of 10^{-6} mm Hg. The absolute values of the accommodation coefficients were obtained by relative measurements with the help of the following simple relation that was found to exist for paraffin hydrocarbons between the accommodation coefficient α , the specific heat per mole at constant pressure for the ideal gas state C_{v0} , and the molecular weight M ,

$$\alpha(C_{v0} + R/2)/M = \text{constant} = 0.352,$$

where R is the gas constant per mole. This equation supports a further relation which can be set up for the mean specific heat between 20° and 140°C for the paraffins by using a few reliable C_{v0} values: $C_{v0} = 0.352M + 1.80$. A combination of both relations gives the simple equation for α of the paraffins:

$$\alpha = c_1 M / (c_1 M + c_2),$$

where $c_1 = 0.352$ and $c_2 = 1.80 + R/2$. The accommodation coefficient for hydrogen was found to be 0.310, in excellent

agreement with earlier experimental values. The accommodation coefficients of ethane and ethylene whose specific heats are known from normal frequencies were found to be equal within a few tenths of a percent; acetylene was found to be 3 percent lower. Specific heats have been calculated for paraffin gases and vapors up to n -heptane by a combination of the results of this work and the specific heat of ethane from the normal frequencies. The specific heats are given to 300°C. Under the assumption of equal accommodation coefficients for paraffins and corresponding olefines based on the accommodation coefficient measurements of ethane and ethylene and on their specific heats, specific heats are given for propylene and n - and isobutylene to 300°C. It was found that the absolute difference between the specific heats of a paraffin and the corresponding olefine decreases with the chain length. The C_{v0} values of the following pairs were found to be equal within the experimental error of one percent: n - and isobutane, n - and isobutylene, methyl acetylene and allene. Approximate values for the mean specific heats between 20° and 140°C are given for methyl acetylene and allene. A discussion is given of the relationship of the present work to spectroscopic work in the field.

INTRODUCTION

THIS paper is part of a broader investigation that is chiefly concerned with an examination of the heterogeneous thermal decomposition of organic molecules by a molecular beam method. During the course of the investigation it was necessary, in order to facilitate the analysis of hydrocarbon mixtures and mixtures of hydrocarbons with hydrogen at pressures of some 10^{-6} mm Hg by the hot wire method, to study the relative accommodation coefficients of various hydrocarbon molecules. This study has disclosed an interesting relationship between the accommodation coefficient α , the molar heat at constant volume for the ideal gas (zero pressure) C_{v0} , and the molecular weight M for paraffin hydrocarbons which makes it possible to determine the true accommodation coefficient of any gas from relative measurements only.

* Presented in part before the American Physical Society at Seattle (Washington), June, 1936.

THEORY OF HEAT CONDUCTION AT LOW PRESSURES

According to M. Knudsen,¹ in agreement with M. v. Smoluchowski,² that part of heat transfer between two surfaces which is due to conduction by the gas molecules at low pressures, provided the mean free path is large compared with the relevant dimensions of the apparatus, may be written for monatomic gases

$$Q = \frac{4}{3(6\pi)^{\frac{1}{2}}} n \bar{\omega} C_v (T_2 - T_1) = \frac{2}{(6\pi)^{\frac{1}{2}}} n \bar{\omega} R (T_2 - T_1), \quad (1)$$

where Q is the heat transfer per unit area per second, n the number of mols per cm^3 , $\bar{\omega}$ the mean molecular velocity, $C_v = (3/2)R$, the specific heat per mole at constant volume and $(T_2 - T_1)$ the temperature difference of the two surfaces.

Analogously we may write for polyatomic molecules according to Knudsen

¹ M. Knudsen, *Ann. d. Physik* (4) **34**, 593 ff (1911).

² M. v. Smoluchowski, *Ann. d. Physik* (4) **35**, 990 (1911).

$$Q = \frac{4}{3(6\pi)^{\frac{1}{2}}} n\bar{\omega}(T_2 - T_1) \left[\frac{3}{2}R + \frac{3}{4}\left(C_v - \frac{R}{2}\right) \right], \quad (2)$$

$$Q = \frac{1}{(6\pi)^{\frac{1}{2}}} n\bar{\omega}\left(C_v + \frac{R}{2}\right)(T_2 - T_1),$$

where the expression in brackets is equal to the sum of the translational part of the specific heat plus $\frac{3}{4}$ of the internal specific heat. The factor $\frac{3}{4}$ expresses the fact that, under the assumption of independent Maxwell distributions of translational and internal energy, a molecule with high translational energy contributes more to the energy transfer than a slow molecule.

Eqs. (1) and (2) hold only if there is no temperature jump between the surfaces and the mean temperature of the gas molecules leaving the surface, i.e., if the temperature difference $(T_2' - T_1)$ of the gas before and after leaving the surface is equal to the difference of temperatures $(T_2 - T_1)$ of the surface and the gas before the collision. Otherwise we have to write, more generally,

$$(T_2' - T_1) = \alpha(T_2 - T_1).$$

The coefficient α was called by Knudsen the accommodation coefficient. Since the present measurements, like most of the earlier work, have been done with a heated wire the dimensions of which are very small compared with the surrounding colder glass tube, the gas acquires the temperature of the outer tube and we may write Eqs. (1) and (2), by introducing the accommodation coefficient α between the heated wire and the gas,

$$Q = \frac{2}{(6\pi)^{\frac{1}{2}}} n\bar{\omega}R\alpha(T_2 - T_1) \quad (3)$$

for monatomic gases and

$$Q = \frac{1}{(6\pi)^{\frac{1}{2}}} n\bar{\omega}\alpha\left(C_v + \frac{R}{2}\right)(T_2 - T_1) \quad (4)$$

for polyatomic gases.

EXPERIMENTAL

As stated in the introduction, the apparatus was not primarily designed for the investigation of accommodation coefficients. The molecular beam method proved, however, to be so appro-

priate for the measurement of accommodation coefficients at extremely low pressures that it may very well be adopted for measurements of this type in the future.

The beam was produced in agreement with the specifications outlined in three important papers on the molecular beam method by O. Stern and collaborators.³ The source aperture was a short channel 0.50 mm long and 0.528 mm in diameter. The image orifice, 26.2 mm away from the source, was a channel ~ 1 mm long and 0.900 mm in diameter. In line with these two orifices was the receiver canal, 62.2 mm away from the entrance to the image orifice. The canal had a conical shape for better definition of the beam although this is not essential for the present part of the investigation. The entrance orifice had a diameter of 0.795 mm, the end of the canal a diameter of 1.60 mm. The canal was 11.96 mm long. Its Knudsen resistance was 5.19 times larger than the resistance of an ideal aperture of the diameter of the entrance orifice, if the latter resistance is taken as

$$R_s = \frac{(2\pi)^{\frac{1}{2}}}{\pi r^2} \text{ and the former as } R_c = \frac{3}{8} \left(\frac{2}{\pi}\right)^{\frac{1}{2}} \int_0^L \frac{dl}{r^3},$$

r being the radius and L the length of the canal.⁴

The maximum gas pressure in the reservoir from which the gas effused was of the order of 0.1 mm Hg and was measured with an accuracy of 0.3 percent by a special manometer previously described.⁵ The two spaces between the three apertures were evacuated by two high speed high vacuum oil diffusion pumps charged with Apiezon oil *B*. The fore vacuum for these two pumps was provided by another oil diffusion pump and finally by a "Cenco Megavac" rotating oil pump. With a reservoir pressure of 0.1 mm Hg, a vacuum of about $2 \cdot 10^{-5}$ mm Hg could be maintained in the first space and better than $1 \cdot 10^{-5}$ mm Hg in the second space. A molecular beam entering an otherwise closed

³ O. Stern, *Zeits. f. Physik* **39**, 751 (1926); Knauer and Stern, *ibid.*, p. 764; Knauer and Stern, *ibid.* **53**, 766 (1929). See also the excellent monography on *Molecular Rays* by Ronald G. J. Fraser (The Macmillan Company, 1931), The Cambridge series of Physical Chemistry.

⁴ M. Knudsen, *Ann. d. Physik* **28**, 76 (1909); see also v. Smolochowski, *ibid.* **33**, 1559 (1910).

⁵ O. Beeck, *Rev. Sci. Inst.* **6**, 399 (1935).

vessel behind the receiver canal will set up a maximum stationary pressure:

$$p_{\infty} = (pa/\pi r^2)k \quad (5)$$

if p is the reservoir pressure, a the area of the source aperture, r the distance of the source aperture from the entrance of the receiver channel and $k = (R_c + R_s)/R_s$, where R_c , R_s are, respectively, the Knudsen resistances of the canal, and of an ideal aperture of the same cross section as the entrance to the canal. Eq. (5) is correct only if the source aperture is ideal (infinitesimally thin), if source and receiver are at the same temperature, and if the molecules in the beam suffer no collisions in the two spaces between the apertures. The first and the last assumptions cannot be realized in practice. We see from Eq. (5) that, under ideal conditions, the pressure p_{∞} is independent of the molecular weight of the gas and of the cross section of the canal. A careful and critical study of all the errors involved led us to the conclusion that a pressure $p = 0.1$ mm Hg in the reservoir produced on the average a maximum stationary pressure $p_{\infty} = 1 \cdot 10^{-6}$ mm Hg in the receiver vessel, which is about 10 times lower than would be expected under ideal conditions. This relationship also varies from gas to gas due to several factors, such as the resistance of the tube leading from the reservoir to the source orifice, the pumping speed, etc., all depending essentially on the mean free path of the gas under consideration. The pressure set up in the receiver vessel by the molecular beam was measured by a highly sensitive Pirani manometer of the type used by Knauer and Stern.³ An exact counterpart of this manometer was placed beside the measuring manometer in the same constant temperature bath. The opening of this manometer led into the same space as the beam manometer. Thus it was subject to the same temperature and pressure fluctuation as the beam manometer. The manometers formed two arms in a balanced sensitive Wheatstone Bridge. The bridge is unbalanced when the molecular beam enters the beam manometer, and the observed galvanometer deflection is for small pressures proportional to the pressure change. The sensitivity of the arrangement used was approximately $2 \cdot 10^{-8}$ mm Hg pressure change per mm deflection of the galvanometer for the

monatomic gas argon. The sensitivity was of course very much higher for large polyatomic molecules.

Let us, for purposes of simplification, introduce the relative sensitivity S which is the galvanometer deflection in cm produced by a reservoir pressure of 0.1 mm Hg. The sensitivity is specific for a given gas. However, it also depends on the reservoir pressure since, as has been pointed out above, the conditions are not ideal. These difficulties have been overcome by measuring the sensitivity S as a function of the reservoir pressure for all gases under consideration. By extrapolation of these sensitivity curves the sensitivity S_0 for the reservoir pressure zero may be obtained. Except for the possibility of a small error due to vapor pressures of the sealing materials used in the apparatus, which might scatter the various gases in the beam by different amounts, the values for S_0 should obey Eq. (5), i.e., the values for S_0 are independent of the pressure p in the reservoir, and the pressure p_{∞} is independent of the molecular weight of the gas.

Thus the values of S_0 may be used directly to find the relative accommodation coefficients of the gases investigated by combining them with Eq. (3) or (4) in which $\bar{\omega}$ is inversely proportional to \sqrt{M} . One may write, for instance,

$$\frac{(S_0)_{\text{gas}}}{(S_0)_A} = \frac{\alpha_{\text{gas}}(M_A)^{1/2}[(C_v)_{\text{gas}} + R/2]}{\alpha_A(M_{\text{gas}})^{1/2}2R},$$

where the subscript A refers to the monatomic gas argon. Then

$$\frac{\alpha_{\text{gas}}}{\alpha_A} = \alpha' = \frac{(S_0)_{\text{gas}}(M_{\text{gas}})^{1/2}2R}{(S_0)_A(M_A)^{1/2}[(C_v)_{\text{gas}} + R/2]}, \quad (6)$$

α' being the accommodation coefficient relative to argon.

Fig. 1 shows the sensitivity S as a function of the reservoir pressure p for all gases and vapors investigated (for hydrogen see Fig. 2). It is evident that the extrapolation of the sensitivity curves to $p = 0$ is permissible only if the individual accommodation coefficients do not change in the pressure interval in which the curve has been established. Reasonable as this assumption may seem because the pressure range is not more than twenty-fold and because the pressure

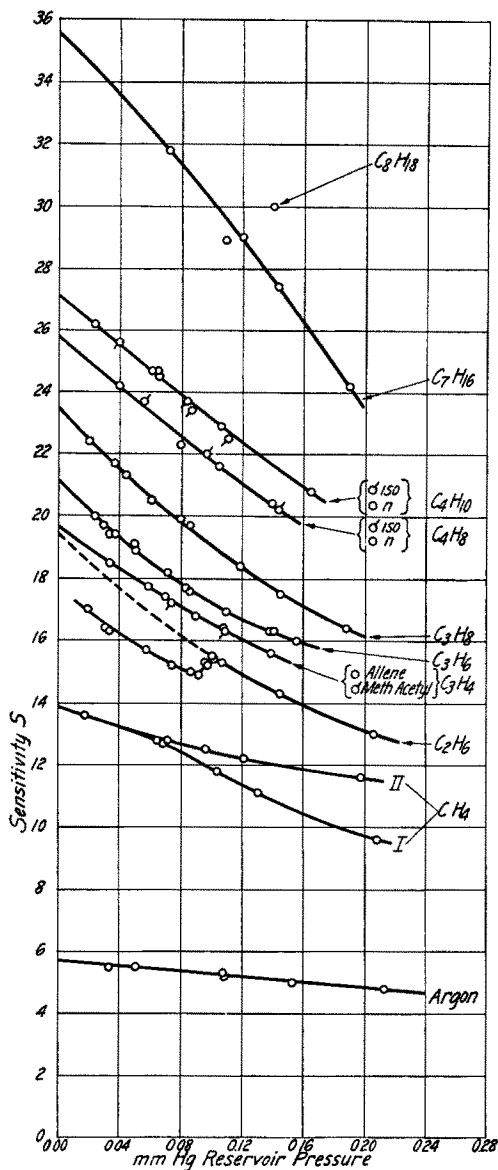


FIG. 1. Sensitivity S (i.e., galvanometer deflection per 0.1 mm Hg gas pressure in the reservoir) plotted against the reservoir pressure.

independence of the accommodation coefficient has been well established in higher pressure regions for various gases by several investigators,⁶ the sensitivity curve of ethane shows a distinct break at a reservoir pressure of about 0.1 mm Hg which corresponds to a pressure rise of about $1 \cdot 10^{-6}$ mm Hg in the manometer vessel, caused by the entering beam. To this must be

⁶ See for instance: Rowley and Bonhoeffer, *Zeits. f. physik. Chemie* B21, 84 (1933).

added an initial pressure which varies also with the reservoir pressure and is probably of the same order of magnitude. The sudden change in the accommodation coefficient of ethane is undoubtedly due to a sudden change of the surface conditions (type of adsorption layer) of the manometer wire. This change is evidently a function of the pressure of the surrounding gas.

Fig. 2 shows the sensitivity curve of ethane on a larger scale together with the sensitivity curves of ethylene and acetylene and two points for hydrogen. While there is no sharp break in the two latter curves, a discontinuity is readily observed in the case of ethylene, and acetylene also follows the same trend. This discontinuity is unique for these three gases. No other gas has shown a similar behavior. It seems that the pressure region was particularly favorable for such an effect with ethane, ethylene and acetylene. The same effect might be expected to occur for larger molecules at still lower pressures or higher temperatures of the manometer wire since the boiling points of these substances are higher. Consequently we have used the extrapolation of that part of the ethylene curve which belongs to the higher reservoir pressures. This extrapolation is in excellent agreement with the general relations derived from our measurements and discussed below.

The influence of the pumping speed on the sensitivity curves is illustrated in the case of methane (Fig. 1). Here two sensitivity curves have been taken with different pumping speeds; curve I with a lower speed than II. Both fall together as expected at low reservoir pressures.

It was found that for paraffins with the exception of methane the values for S_0 are, as shown in Table I, proportional to the square root of the molecular weight to a surprising degree of accuracy.

In combining this result with Eq. (4) and in setting Q proportional to S_0 , i.e., proportional to \sqrt{M} , and $\bar{\omega}$ inversely proportional to \sqrt{M} , we arrive at the simple equation:

$$\alpha(C_v + R/2)/M = \text{const.} \quad (7)$$

In order to evaluate Eqs. (6) and (7) the specific heat C_v of the polyatomic gases under investigation must be known. To obtain high sensitivity, the temperature of the gauge wire

was chosen considerably higher than the temperature of the gauge wall. We therefore have to consider the mean specific heat of the gas molecules between these two temperatures. The mean temperature of the wire itself was measured by its resistance, the temperature dependence of which had been established by a special calibration. This calibration was made by placing the gauge in constant temperature baths of various temperatures and measuring its resistance in a high-sensitive bridge with the lowest possible current passing through the bridge. By varying the current slightly, a curve was established whose extrapolation to zero current gave the correct resistance for the temperature of the bath.

Throughout the investigation the gauge wires were operated at a mean temperature of 140°C and the gauge walls were kept at 20°C. The gauges were Pyrex glass tubes about 12 cm long and 1 cm internal diameter, each containing a nickel ribbon 20 cm long, 50 μ wide and 3 μ thick. The nickel was shown by conductivity measurements to be almost pure. Its surface was brilliant like that of a platinum wire. The wire was not handled, and was cleaned only with alcohol and distilled water to remove the flux used in soldering the wire to its terminals. The wire was not heated above the operating temperature of 140°C. We may call the nickel surface "ordinarily clean." The mean specific heat between 20° and 140° was calculated from the normal frequencies⁷ for methane, ethane, ethylene and acetylene, by the Planck-Einstein function. A value for butane at 80°C was taken from a recent investigation by Sage and Lacey.⁸ A value for propane by the

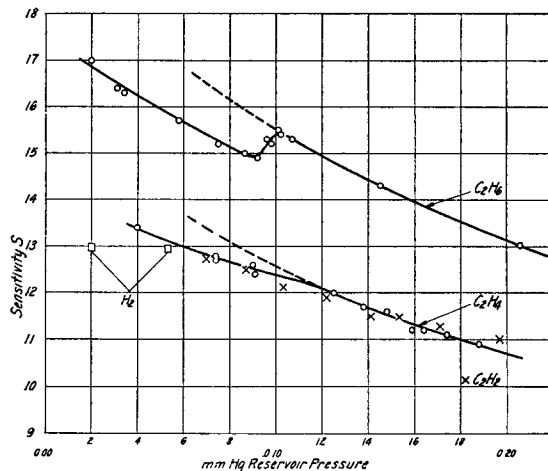


FIG. 2. Sensitivity S (i.e., galvanometer deflection per 0.1 mm Hg gas pressure in the reservoir) plotted against the reservoir pressure.

same authors was discarded because of its uncertainty.

Remembering that Soddy and Berry,⁹ Knudsen¹ and others have shown previously that on ordinarily clean surfaces the accommodation coefficient rapidly approaches unity with increasing molecular weight, we see from Eq. (7) that the increase of C_v must be proportional to M for high molecular weight paraffins. This proportionality, which is demanded by Eq. (7) is in fact approximately true for the specific heat of the three available lower paraffins, methane, ethane and butane and has also been observed by Lewis and McAdams.¹⁰ It is needless to say that since we are concerned with specific heats at extremely low pressures, we are dealing essentially with C_{v0} values, i.e., with specific heats of the ideal gases. Calculation from normal

⁷ The following normal frequencies expressed in wave numbers were used:

CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
1304(3x)	600(2x)	730	750(2x)
1520(2x)	729(2x)	950	827(2x)
2915	1975	1097	993
3020(3x)	3277	1110	1370
	3370	1160	1460(3x)
		1342	1480(2x)
		1444	2890(2x)
		1623	2899(2x)
		2090	2955
		3019	3020
		3110	
		3240	

For references on this subject see: A. Eucken and A. Bertram, *Zeits. f. physik. Chemie* **B13**, 361 (1936), and E. Teller and B. Topley, *J. Chem. Soc. London*, 885 (1935).

⁸ B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **27**, 1484 (1935). The authors give a straight line between 60° and 220°F. Since in case of ethane the mean specific heat between 20° and 140°C is very close to the true specific

TABLE I.

	S_0	\sqrt{M}	S_0/\sqrt{M}
CH ₄	13.9	4.00	3.48
C ₂ H ₆	19.5	5.48	3.56
C ₃ H ₈	23.5	6.64	3.54
C ₄ H ₁₀	27.1	7.63	3.55
C ₇ H ₁₆	35.6	10.01	3.56

heat at 80°C, we have chosen for butane the true specific heat value at 80°C for reference in order not to depend on the slope of the line which fits the experimental points far better in the neighborhood of 80°C than at lower temperatures.

⁹ F. Soddy and A. J. Berry, *Proc. Roy. Soc.* **A83**, 254 (1910); *ibid.* **A84**, 576 (1911).

¹⁰ W. K. Lewis and W. H. McAdams, *Chem. and Met. Eng.* **36**, 336 (1929). See also p. 689 of this paper.

frequencies give C_{v_0} values directly. The C_{v_0} value for butane was calculated from Sage and Lacey's measurements by means of Berthelot's equation of state. The almost perfect proportionality of the increase with M of those three values for C_{v_0} is at least a good support for the deductions made from Eq. (7). We feel, however, that there are good reasons for believing the methane value to be slightly lower (see discussion below). The equation for C_{v_0} was set up, therefore, by use of the ethane and butane values only. Thus we arrive at an equation representing the mean specific heat of the paraffins, between 20° and 140°C, in terms of the molecular weight.

$$C_{v_0} = 0.352M + 1.80. \quad (8)$$

Next α' has been calculated according to Eq. (6) for all cases in which the specific heat is known or can be calculated from Eq. (8). The values for α' are given in Table II.

By introducing the values for α' and for C_{v_0} into Eq. (7) we find for paraffins the relation

$$(C_{v_0} + R/2)\alpha' = 0.388M. \quad (9)$$

and by combining Eqs. (8) and (9)

$$\alpha' = 0.388M / (0.352M + 1.80 + R/2).$$

For large M , we obtain

$$\lim_{M \rightarrow \infty} \alpha' = 0.388/0.352$$

and since this value must be identical with the true accommodation coefficient $\alpha = 1$, we obtain $\alpha = (0.352/0.388)\alpha'$,

$$\begin{aligned} \text{or } \alpha &= \frac{0.352}{0.388} \left(\frac{0.388M}{0.352M + 1.80 + R/2} \right) \\ &= \frac{0.352M}{0.352M + 1.80 + R/2}. \end{aligned}$$

TABLE II.

Gas	α'	α
Argon	1	0.90 ₇
Hydrogen	0.34 ₂	0.31 ₀
Methane	0.73 ₇	0.66 ₉
Ethane	0.87 ₃	0.79 ₃
Ethylene	0.87 ₂	0.79 ₁
Acetylene	0.84 ₄	0.76 ₅
Propane	0.93 ₄	0.84 ₇
<i>n</i> -Butane } Isobutane }	0.97 ₂	0.88 ₂
<i>n</i> -Heptane	1.02 ₃	0.92 ₈

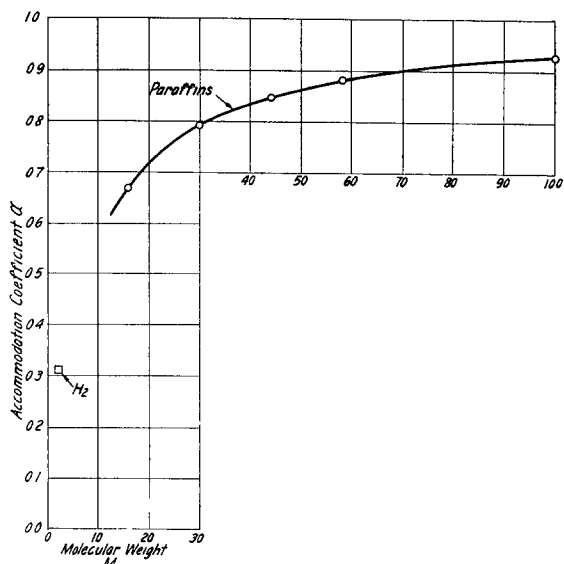


FIG. 3. The accommodation coefficients of the paraffins and of hydrogen plotted against the molecular weight.

The values for α are given in Table II. In Fig. 3, α for the paraffins is plotted against the molecular weight. α for hydrogen is added for comparison.

SPECIFIC HEATS

In examining Table II we find equal accommodation coefficients for *iso*- and normal butane and for ethane and ethylene. The former was derived from the fact that the sensitivity curve (Fig. 1) is the same for both gases. Strictly speaking, this only means that in both cases the product $\alpha \cdot (C_{v_0} + R/2) = \text{constant}$. If, therefore, we assume α to be the same for *iso*- and *n*-butane, we must conclude that C_{v_0} is also the same. In view of the fact that ethane and ethylene have been shown to have the same accommodation coefficient, equality of accommodation coefficients of the isomers of butane seems almost certain. Furthermore, the assumption seems justified that corresponding paraffins and olefins have the same accommodation coefficient. Again, since isobutylene and normal butylenes¹¹ lie on the same sensitivity curve, their accommodation coefficients and specific heats are presumably equal. The same sensitivity curve has been observed for allene and for methyl acetylene. Their absolute value, however,

¹¹ A mixture of 25 percent α -butylene and 75 percent β -butylene was used.

may not be obtained with the same certainty as the absolute values of the olefines, because we do not feel justified in setting their α equal to that of propane and propylene due to the fact that the accommodation coefficient of acetylene is about 3 percent lower than that of ethane and ethylene. The discrepancy will probably be less in the case of higher molecular weights and an approximate value of the specific heat of methyl acetylene and allene may be obtained by setting their accommodation coefficient equal to that of propane and propylene. In Table III are given the mean specific heats between 20° and 140°C at constant volume for the ideal gas state of all gases and vapors investigated.

This, however, is not the only information on specific heats that may be gained from these observations. In case of the paraffins, Eqs. (7) and (8) have been established for mean specific heats between 20° and 140°C. It follows therefore that the increase of the true specific heats at any temperature in this temperature interval must also be proportional to the molecular weight. Knowing accurately from spectroscopic data, in the case of ethane the relation of specific heat to temperature we are able to calculate true specific heats of all other paraffins at any temperature. Assuming that the laws established in the temperature region between 20° and 140°C will hold likewise at higher temperatures, we have calculated the specific heats of the paraffins up to 300°C, using ethane as reference. Furthermore, the specific heat of ethylene being known from spectroscopic data, we find by comparison of the curves for ethane and ethylene, that their ratio stays almost constant. At 300°C the ratio differs only 2 percent from its value at 0°C. Such a discrepancy necessarily will be smaller for larger paraffin molecules and their respective olefines.

Using Eq. (5) we arrive at the specific heat of the paraffins at any temperature by means of the relation

$$C_t = ((C'_t - 1.80)/(C'_{20 \text{ to } 140} - 1.80)) \times (C_{20 \text{ to } 140} - 1.80) + 1.80, \quad (10)$$

where C_t is the specific heat per mole of the gas considered, at zero pressure and at the temperature t , and C_{20-140} is the mean specific heat between 20° and 140°C of the same gas; C' refers to ethane, the reference gas, and 1.80 is an experi-

mental constant. The values for the olefines are obtained by using the experimental ratio of paraffins and their respective olefines found for the mean specific heats between 20° and 140°C.

In Table IV are given the C_{v_g} values for C_nH_{2n+2} up to $n=7$, and also ethylene, propylene and acetylene. Further values for paraffins may be calculated from Eqs. (8) and (10) using the corresponding ethane value as standard.

Table V gives the specific heat C_p at constant pressure (one atmosphere) calculated with the help of Berthelot's equation of state. This equation is known to hold well for hydrocarbon vapors at pressures sufficiently below the critical pressure, which is true for all vapors under consideration. From Berthelot's equation we derive:

$$C_p = C_{v_0} + R + (81/32)R(T_c/T)^3 p/p_c,$$

where T_c and p_c are the critical temperature and the critical pressure.

DISCUSSION

Paraffins

A discussion of the theoretical aspects of the law governing the accommodation coefficients of the paraffins will be postponed until data for various gas temperatures and various surface temperatures have been completed.

Hydrogen

The value for the accommodation coefficient α of hydrogen is in excellent agreement with values recently obtained by other investigators on various surfaces, especially with the value obtained

TABLE III.

Gas	C_{v_g} mean 20° to 140°C	Remarks
CH ₄	7.17	from normal frequencies
CH ₄	7.25	this investigation (Eqs. (7) and (8))
C ₂ H ₆	12.35	from normal frequencies (reference value)
C ₃ H ₈	17.25	this investigation (Eq. (8))
<i>n</i> -C ₄ H ₁₀	22.2	Sage and Lacey's (reference value)
<i>iso</i> -C ₄ H ₁₀	22.2	assuming equal accommodation coefficient for <i>n</i> - and <i>iso</i> -C ₄ H ₁₀
<i>n</i> -C ₇ H ₁₆	37.0	this investigation (Eq. (8))
C ₂ H ₄	9.55	from normal frequencies
C ₃ H ₆	15.09	assuming equal accommodation coefficient for C ₃ H ₈ and C ₃ H ₆
<i>n</i> - } C ₄ H ₈	20.5	assuming equal accommodation coefficient for <i>n</i> -C ₄ H ₁₀ and <i>iso</i> -C ₄ H ₁₀
<i>iso</i> - }		
C ₂ H ₂	9.50	from normal frequencies
allene } C ₃ H ₄	13.5	assuming equal accommodation coefficient for C ₃ H ₈ and C ₃ H ₄
methyl acetylene }		

TABLE IV.

$t^{\circ}\text{C}$	C_v in cal./mole $^{\circ}\text{C}$			
	0	100	200	300
CH_4	6.34	7.38	8.76	10.19
C_2H_6	9.86	12.98	16.06	18.78
C_3H_8	7.70	10.05	12.32	14.32
C_4H_{10}	8.15	9.78	10.89	11.73
C_5H_{12}	13.59	18.16	22.70	26.69
C_6H_{14}	11.89	15.89	19.82	23.30
C_7H_{16}	17.37	23.40	29.34	34.60
C_8H_{18}	16.04	21.61	27.09	31.95
C_9H_{20}	21.12	28.60	35.98	42.51
$\text{C}_{10}\text{H}_{22}$	24.87	33.80	42.62	50.42
$\text{C}_{11}\text{H}_{24}$	28.63	39.01	49.27	58.32

TABLE V.

$t^{\circ}\text{C}$	C_p (at 1 atmos.) in cal./mole $^{\circ}\text{C}$			
	0	100	200	300
CH_4	8.37	9.39	10.75	12.18
C_2H_6	11.99	15.02	18.07	20.78
C_3H_8	9.80	12.08	14.33	16.32
C_4H_{10}	10.29	11.83	12.91	13.73
C_5H_{12}	15.86	20.26	24.74	28.71
C_6H_{14}	14.14	17.98	21.86	25.31
C_7H_{16}	19.89	25.59	31.43	36.64
C_8H_{18}	18.61	23.82	29.19	34.00
C_9H_{20}	23.93	30.93	38.19	44.57
$\text{C}_{10}\text{H}_{22}$	27.93	36.26	44.89	52.51
$\text{C}_{11}\text{H}_{24}$	32.07	41.56	51.53	60.46

by Rowley and Evans¹² on an ordinarily clean iron surface at the same temperature as was used in this investigation. Their value is 0.31. Rowley and Evans by comparing their results with others came to the conclusions that they had measured the accommodation coefficient on an iron surface covered with adsorbed hydrogen. This conclusion was based on the fact that approximately the same value was found by other investigators on various materials. It seems most likely that at a surface temperature of 140°C a gas layer was present on the nickel used in this investigation or on the iron used by Rowley and Evans. Since this layer should not be affected by the hydrogen pressure at a moderately high temperature of the surface, it is not astonishing that the value found in this investigation with hydrogen pressures of some 10^{-6} mm Hg is in agreement with the value of Rowley and Evans at approximately 0.025 mm Hg. Earlier work of Rowley and Bonhoeffer, for instance, has shown the accommodation coefficient of hydrogen on platinum to be independent of the pressure between 0.03 and 0.3 mm Hg.

It must be emphasized that a direct measurement of the accommodation coefficient at pressures of 10^{-6} mm Hg would lead to great experimental difficulties since the energy radiated from the surface at 140°C is about 10^4 times larger than that resulting from the collision of the gas molecules. By means of the relations found for the paraffin series, the true accommodation coefficient for hydrogen or any other gas at 10^{-6} mm Hg was found by relative measurement only.

Specific heats and spectroscopy

The observed proportionality between the increase of C_v and M for the paraffins suggests at once a simple relationship of infrared and Raman spectra in the paraffin series. A glance at the graphic presentation of the Raman lines from n -butane to n -dodecane reveals indeed striking similarity and comparative simplicity. This agreement is not only true for frequencies assigned to C—H bonds and C—H deformations which lie above 1100 cm^{-1} , but is surprisingly good in the range of the chain oscillations proper. Propane and ethane show a much simpler Raman spectrum. The intimate relation between ethane, propane and n -butane, however, may be readily shown by an empirical summation rule of Kohlrausch and Barnés,¹³ as applied to the C—C frequencies. This rule is applicable also to cyclopropane, isobutane and neopentane (tetramethylmethane). The rule is given by the equation:

$$\bar{\nu} = ((1/(s-1)) \sum \nu_i^2)^{1/2},$$

where $\bar{\nu}$ is a frequency characteristic for C—C chains. In making the summation, frequencies of 2 or 3 fold degeneracy must be taken 2 or 3 times. $s-1$ is the number of similar valency bonds. Kohlrausch and Köppl found that the gases named above satisfy the rule with an error of one percent.

A few remarks are necessary in respect to methane. In spite of the fact that Eqs. (8) and (9) seem to hold for methane within a few percent, there are good reasons for believing that the methane value is slightly lower.

¹³ K. W. F. Kohlrausch and D. Barnés, Ann. Soc. Españ. Fis. Quím. **30**, 733 see also: K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934), especially p. 218 ff.

¹² H. H. Rowley and W. V. Evans, J. Am. Chem. Soc. **57**, 2059 (1935).

At 0°C the contribution of the oscillatory degrees of freedom to the specific heat is very small in the case of methane, and although this contribution still decreases towards lower temperatures, it is almost constant in the close neighborhood of $6R/2$. Towards lower temperatures the methane value is therefore too high and Eq. (8) must break down completely in the case of methane. At higher temperatures the value for the specific heat of methane which satisfies Eq. (8) is slightly greater than the value calculated from normal frequencies. In Fig. 4 are given curves for ethane and methane as calculated from normal frequencies and the curve for methane given by Eq. (8). It is readily seen that below 0°C. Eq. (8) breaks down entirely. As to the discrepancy at higher temperatures the following explanation may be offered without going into the details of this complex problem. Let us consider only the C—H frequencies and the C—H deformation frequencies. If the specific heat of the paraffins is proportional to M , we may assume that the contribution of the C—H frequencies and the C—H deformation frequencies is additive within the limit of error of our investigation. This can only mean that these oscillations are well localized and practically independent of the chain length, or in other words that we have a constant binding force. The group of C—H valence frequencies and deformation frequencies in the Raman spectra is indeed remarkably constant, especially from butane upwards.

There are two frequency regions of C—H deformation frequencies for paraffin molecules from ethane upwards, one region at about 750 cm^{-1} and the other about 1400 cm^{-1} . The frequency 750 cm^{-1} seems definitely to be associated with a bond angle that only occurs when two or more carbon atoms are present, probably the angle C—C—H.

Any attempt, therefore, to extrapolate to methane the measurements with higher paraffins would include the consideration of the deformation frequency at about 750 cm^{-1} . The number of frequencies depending on the bond angle C—C—H decreases according to: 10 for butane, 7 for propane, 4 for ethane, which would give the extrapolated value 1 for methane. The true value for methane is, however, zero. The contribution

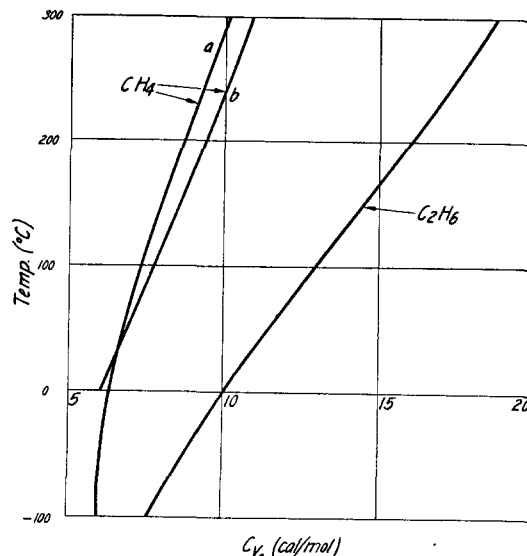


FIG. 4. The specific heat in cal. per mole and °C for the ideal gas state calculated for ethane and methane (curve *a*) from the normal frequencies and the values for methane (curve *b*) calculated from Eq. (8).

of this excess frequency to the specific heat is in rough agreement with the discrepancy between the values from normal frequencies and the value obtained by Eq. (8), the latter value being too high. This shows clearly that Eq. (8) must not be expected to hold for methane.

It is noteworthy that the absolute value of the difference between the specific heat of a paraffin and the respective olefine becomes smaller with increasing molecular weight. This indicates a definite effect of the chain length on the double bond. The only (and an apparently safe assumption), in obtaining the C_{v_0} value for the olefines is that of equality of the accommodation coefficients for paraffins and respective olefines; no other errors are possible. A similarly pronounced effect cannot be observed in Raman and infrared spectra, but this might be due to the fundamentally different method of excitation.

Special mention should also be made to the equality of C_{v_0} for the following pairs: *iso* and normal butane, *iso* and *n*-butylene, methyl acetylene and allene. In the latter case two double bonds are substituted for one single and one triple bond without altering the specific heat within the limits of the experimental error of one percent.

While it is realized that this discussion is incomplete from the spectroscopic standpoint, it is,

nevertheless, hoped that the specific heats and their simple relationships now presented will contribute considerably to the proper assignment of fundamental frequencies to the higher paraffins and by so doing will provide the foundation for a correct direct calculation from the normal frequencies of the specific heat of many higher hydrocarbons at higher temperatures.

Sources of error

Apart from the fact that the limit of error of the molecular beam measurements has been found to be one percent, thus establishing the proportionality of $\alpha(C_v + R/2)$ with M to within one percent, the actual equation for C_v , Eq. (8), has been set up by the use of the specific heat value of ethane (from normal frequencies)⁷ and *n*-butane (Sage and Lacy).⁸ Inasmuch as the value of Sage and Lacy may be slightly in error, all other derived values may show about the same relative error. We have, however, confidence in their value for *n*-butane since it was obtained by an adiabatic expansion method which Eucken and collaborators¹⁴ have used previously with much success. We furthermore call attention to specific heat values for the paraffins obtained by Lewis and McAdams¹⁰ by a flow method not designated in detail. Inasmuch as the flow method is known to introduce systematic errors easily, it is not astonishing that they find C_p values at 50°C for methane and ethane which are about 1.2 calories

larger than those from spectroscopic data. However, they find in agreement with this work an increase in specific heat of the paraffins from methane to butane, which is, as they prefer to state, proportional to the number of carbon atoms. If their error is indeed systematic, as may be expected, their values should give the same slope as the values obtained from this investigation. This is actually the case within one percent accuracy, which speaks for the correctness of Sage and Lacy's value for *n*-butane.

As may be seen above, the accuracy of the values for the olefines depends on the accuracy of the values for the respective paraffins and at higher temperatures it depends also on the assumption that at any temperature the ratio of the specific heats of an olefine and the respective paraffin is constant, an assumption which is practically fulfilled in the case of ethane and ethylene as has been stated above in more detail.

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¹⁴ A. Eucken and K. von Lüde, *Zeits. f. physik. Chemie* **B5**, 413 (1929); A. Eucken and A. Parts, *ibid.* **B20**, 184 (1933).

An Elementary Deduction of Gibbs' Adsorption Theorem

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1. INTRODUCTION

IN the thermodynamics of surfaces there is no theorem more important than that known as "Gibbs' adsorption theorem," which determines how the surface tension of a solution varies when the composition is varied at constant temperature. Its derivation by Gibbs has all the logical conviction and elegance characteristic of Gibbs.

But the abstract character of his proof makes it difficult to follow by anyone not thoroughly conversant with Gibbs' methods. Owing to the numerous applications of the theorem to all branches of surface chemistry and particularly colloid chemistry it is very desirable to have a more elementary proof.

Various attempts in this direction have already