# Gas-Solid Interaction

## III. Energy of Adsorption of Some Saturated Hydrocarbons on $\gamma$-Aluminium Oxide *, **

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The heats of adsorption on weakly activated $\gamma$-aluminium oxide for a number of linear alkanes (from n-butane to n-nonane) and for 2.2.4-trimethylpentane have been determined by GSC and extrapolated to zero surface coverage.

The dependance of the adsorption energy on the number of carbon atoms is discussed on the basis of the bidimensional gas model: it is shown that the interactions of the adsorbates with the oxidic surface are mainly due to London dispersion forces.

Gas-solid interactions occurring at very low surface coverages[1], such as those attainable by gas-solid chromatography are of primary interest. For homogeneous surfaces the heats of adsorption measured by GSC agree satisfactorily with values obtained by conventional methods (e. g., calorimetric) at much higher coverages and lower temperatures[2, 3]. On the contrary, the results obtained by GSC technique on heterogeneous surfaces at low temperatures are liable to be somewhat in excess, since in such conditions adsorption takes place almost entirely on the more energetic sites[4]. As, however, most solids have heterogeneous surfaces and, on the other hand, the higher coverages which are necessary with calorimetric methods can introduce other errors due to adsorbate-adsorbate interactions, GSC can be considered a very suitable method also for heterogeneous solids, if the operating temperature is high enough to smooth out the heterogeneity effects.

One of the previous works[5] revealed that the apparent dielectric constant of cyclohexane adsorbed on $\gamma$-$Al_2O_3$, contrary to the benzene case, is not affected by the contact with the oxide layer, since the polarizability of cyclohexane appeared to be the same in the monolayer as in the liquid-like state in capillaries. Assuming this polarizability to be practically the same as for pure liquid, the observation that the slopes of the dielectric isotherms for cyclohexane and for benzene (in the capillary condensation range) were coarsely in the same ratio as the pure liquid dielectric constants, suggest that in this range both adsorbates practically show contributions from their similar electronic polarizations only. On the contrary, the remarkable increase in the slope of the benzene dielectric isotherm in the monolayer region, where molecules are in close contact with the oxidic surface, might be due to the occurrence of other polarizability terms, as arising, e. g., from interaction of surface charged groups with the benzene $\pi$-electron system.

In this connection it is interesting to verify: 1) whether the interaction energy displayed in the adsorption of saturated molecules may be accounted for by dispersion forces only; 2) whether with unsaturated molecules other types of interactions are involved, and 3) how such interactions are affected by increasing unsaturation. For these purposes, the measurements by GSC of the heats of adsorption of a few series of hydrocarbon adsorbates on the same adsorbent already employed in previous works[5], i. e. heterogeneous $\gamma$-$Al_2O_3$, have been started. Available data for such systems are still very scanty.

In the present paper the results are reported and discussed for six linear chain paraffinic hydrocar-

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* Parts I and II, Z. Naturforsch. **22 a**, 203, 355 [1967].

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[1] See, e. g., S. ROSS and J. P. OLIVIER, On Physical Adsorption, Interscience Publ. Co., New York 1964, p. xi.

[2] S. ROSS, J. K. SAELENS, and J. P. OLIVIER, J. Phys. Chem. **66**, 696 [1962].

[3] R. L. GALE and R. A. BEEBE, J. Phys. Chem. **68**, 555 [1964].

[4] S. ROSS, Physical Adsorption by Homogeneous and Heterogeneous Solid Surfaces, in L. J. BONIS and H. H. HAUSNER Ed., Fundamental Phenomena in the Material Science, Plenum Press, New York 1966, p. 109 ff.

[5] M. SANESI and V. WAGNER, Z. Naturforsch. **22 a**, 355 [1967].

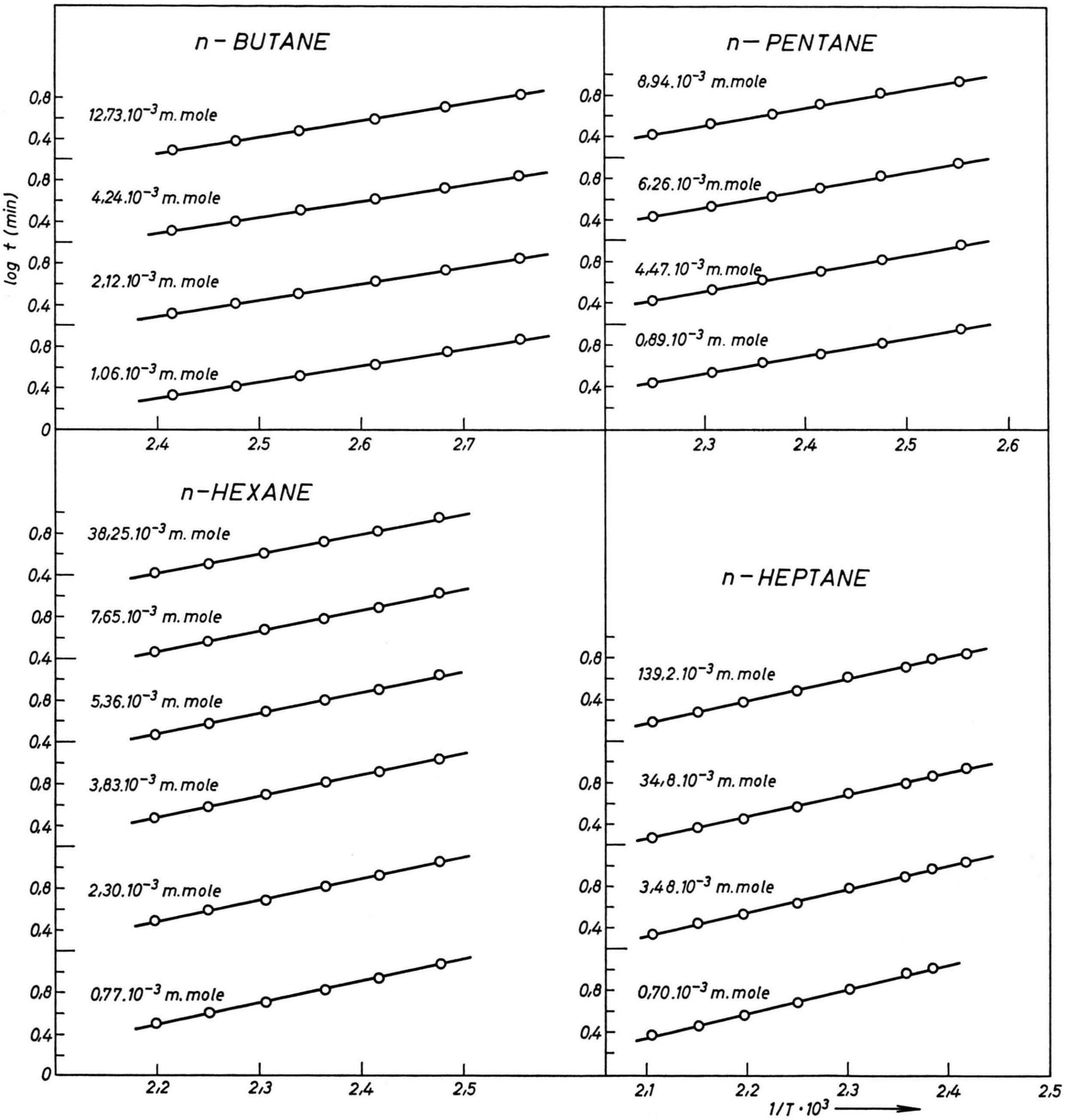

Fig. 1. Plots of decimal logarithms of retention times $t$ vs. reciprocal absolute temperature $T$ for n-butane, n-pentane, n-hexane and n-heptane.

bons (n-butane to n-nonane) and one branched chain hydrocarbon (2.2.4-trimethyl-pentane), while data for other series will be referred to in a next paper.

## Experimental

*Materials.* All of the adsorbates were original FLUKA products of "Puriss" grade (quoted purity $\geqq 99.9$ mole %).

The adsorbent was a sample of the same B.D.H. $\gamma$-alumina "for chromatographic adsorption analysis", used in both previous works [5]. Chemical and spectroscopical analysis gave the following results: water loss in air at 150 °C: 5.07%; the same at 1100 °C: 8.02%; $CO_3^{--}$: 0.35%; alkali-, earth alkali- and transition metals: from 100 to 1 ppm; halogens: $\leqq 20$ ppm.

*Apparatus and procedure:* Retention times were measured with a commercial gas-chromatograph equip-

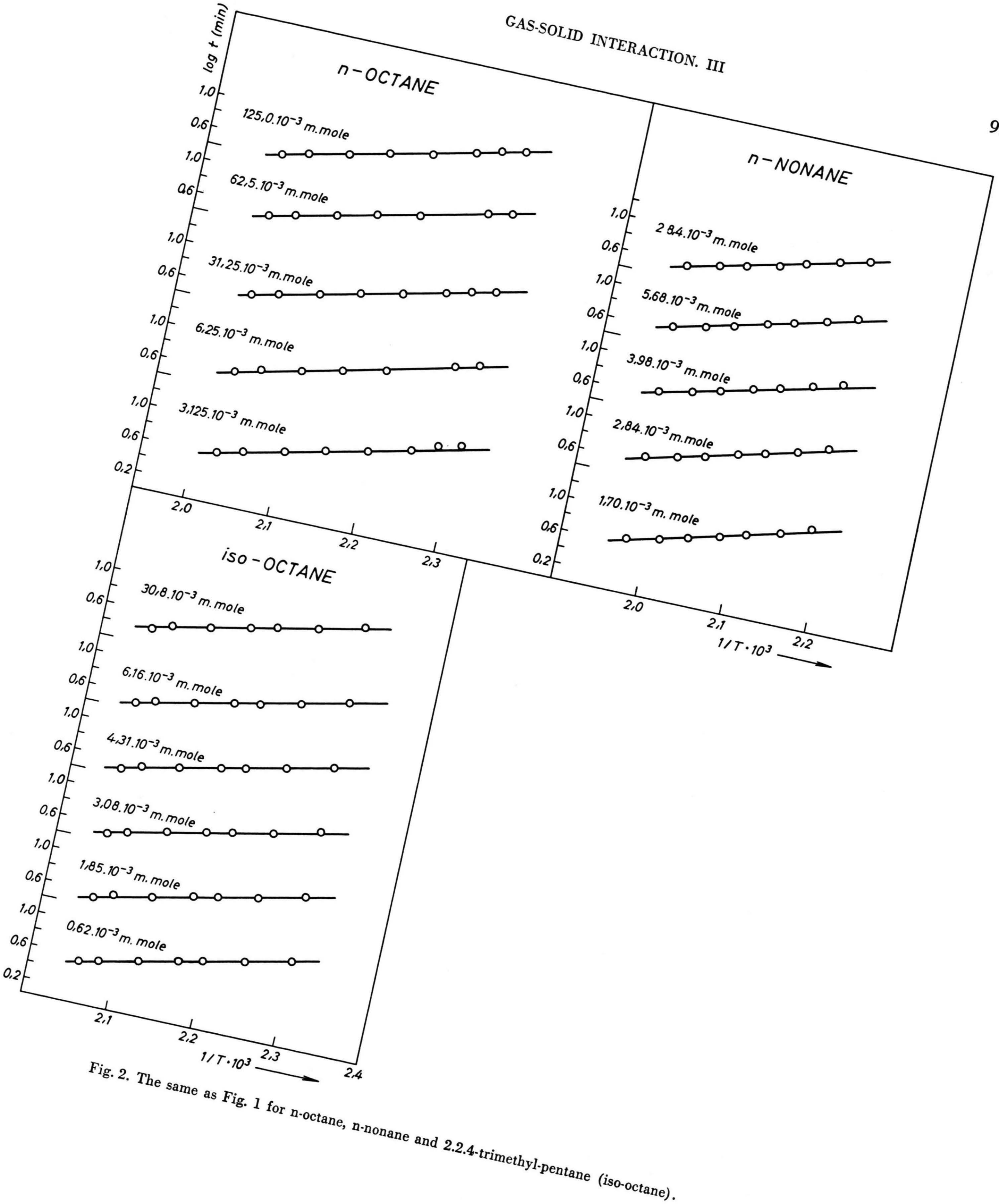

Fig. 2. The same as Fig. 1 for n-octane, n-nonane and 2.2.4-trimethyl-pentane (iso-octane).

ped with thermoconductivity detector (Fractovap Mod. B/f from C. Erba S.p.A.). Temperatures inside the column oven were detected to ± 0.2 °C by means of a Chromel-Alumel thermocouple (calibrated against a NBS certified platinum resistance thermometer) placed at close contact with the column.

The flow-rate measuring device was thermostated at (25 ± 0.1) °C. The pressure ahead the column was read to ± 0.02 kg/cm$^2$ by means of a manometer included in the apparatus; and that behind the column was assumed to be 1 atm.

The carrier gas flow-rate was held constant throughout the measuring runs on one adsorbate. Experimental conditions are summarized in Table 1.

Carrier gas: hydrogen
Column: stainless steel, length 1 m, i.d. 0,6 cm

| Adsorbate | Temperature range [°C] | Flow rate [ml/min] | Pressure drop range [atm] |
|---|---|---|---|
| n-butane | 90—140 | 50 | 0.25—0.31 |
| n-pentane | 120—170 | 50 | 0.30—0.37 |
| n-hexane | 130—180 | 75 | 0.45—0.53 |
| n-heptane | 140—200 | 140 | 0.77—0.91 |
| n-octane | 160—220 | 100 | 0.67—0.79 |
| n-nonane | 185—230 | 140 | 0.88—0.99 |
| iso-octane | 160—210 | 100 | 0.62—0.74 |

Table 1. Gas-chromatographic conditions.

For each compound, retention times at different chosen temperatures were measured with increasing amounts of injected sample. The retention times, referred to those of injected samples of non adsorbed air, were corrected for the pressure drop across the column and for the temperature difference between the column and the flow meter [6]. All adsorbates, except n-butane, were sampled in liquid form and injected by means of conventional microsyringes. The n-butane was sampled by a gas-tight microsyringe.

*Results.* The experimental results are reported in Figs. 1 and 2 as $\log t$ vs. $1/T$ ($t$ in minutes and $T$ in °K). From the slopes of the straight-lines appearing in these plots, the heats of adsorption, $Q_a$, were calculat-

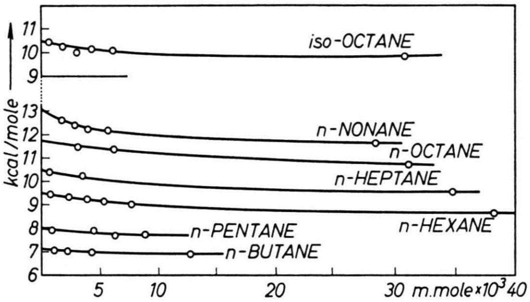

Fig. 3. Change of the chromatographic heats of adsorption with injected sample amount.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| n-butane | µmole | 1,06 | 2,12 | 4,24 | 12,73 | | |
| | $Q_a$ | 7,03 | 7,00 | 6,96 | 6,90 | | |
| | $S_Q$ | 0,08 | 0,07 | 0,05 | 0,07 | | |
| n-pentane | µmole | 0,89 | 4,47 | 6,26 | 8,94 | | |
| | $Q_a$ | 7,91 | 7,86 | 7,70 | 7,73 | | |
| | $S_Q$ | 0,16 | 0,17 | 0,14 | 0,12 | | |
| n-hexane | µmole | 0,77 | 2,30 | 3,83 | 5,36 | 7,65 | 38,25 |
| | $Q_a$ | 9,46 | 9,34 | 9,23 | 9,13 | 9,03 | 8,69 |
| | $S_Q$ | 0,20 | 0,23 | 0,17 | 0,16 | 0,18 | 0,27 |
| n-heptane | µmole | 0,70 | 3,48 | 34,8 | 139,2 | | |
| | $Q_a$ | 10,38 | 10,23 | 9,68 | 9,59 | | |
| | $S_Q$ | 0,26 | 0,14 | 0,10 | 0,17 | | |
| n-octane | µmole | 3,13 | 6,25 | 31,25 | 62,5 | 125,0 | |
| | $Q_a$ | 11,48 | 11,38 | 10,77 | 10,55 | 10,55 | |
| | $S_Q$ | 0,33 | 0,22 | 0,07 | 0,14 | 0,11 | |
| n-nonane | µmole | 1,70 | 2,84 | 3,98 | 5,68 | 28,40 | |
| | $Q_a$ | 12,66 | 12,43 | 12,25 | 12,20 | 11,65 | |
| | $S_Q$ | 0,36 | 0,38 | 0,23 | 0,20 | 0,17 | |
| iso-octane | µmole | 0,62 | 1,85 | 3,08 | 4,31 | 6,16 | 30,80 |
| | $Q_a$ | 10,45 | 10,24 | 9,99 | 10,14 | 10,11 | 9,86 |
| | $S_Q$ | 0,15 | 0,23 | 0,20 | 0,19 | 0,16 | 0,17 |

Table 2. Heats of adsorption, $Q_a$, and standard deviations, $S_Q$, (kcal/mole) measured for different sample amounts.

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[6] A. T. James and A. J. Martin, Biochem. J. London **50**, 679 [1952].

[7] These have been calculated according to Y. Beers (Theory of Error, Addison Wesley Publ. Co., Reading, Mass. 1958, pp. 37 ff.) by the following formula:

$$S_Q = 4.576 \left( \frac{\sum \delta_n^2}{h-2} \right)^{1/2} \left( \frac{h}{h \sum (1/T_n)^2 - (\sum 1/T_n)^2} \right)^{1/2}$$

where $\delta_n$ is the deviation of the $n$-th measurement from the straightline $\log t = a + b/T$ calculated by the least square method, and $h$ is the number of the experimental points.

ed in the usual way. The values are reported in Table 2, together with the standard deviations, $S_Q$[7]. The $Q_a$ values reported in Table 2 were plotted against the adsorbate amount (Fig. 3), thus allowing extrapolation to zero coverage. The extrapolated values are listed in Table 3.

| Adsorbate | $Q_a$ [kcal/mole] on: | | | % difference referred to $\gamma$-$Al_2O_3$ | |
|---|---|---|---|---|---|
| | $\gamma$-$Al_2O_3$[a] | $SiO_2$[b] | MgO[c] | $SiO_2$ | MgO |
| n-butane | 7.08 | 6.42 | | − 9.3 | |
| n-pentane | 8.00 | 7.65 | | − 4.4 | |
| n-hexane | 9.50 | 8.88 | 9.40 | − 6.5 | − 1.0 |
| n-heptane | 10.50 | 10.11 | 11.30 | − 3.7 | + 7.6 |
| n-octane | 11.75 | 11.34 | 12.40 | − 3.5 | + 5.5 |
| n-nonane | 13.10 | 12.57 | | − 4.0 | |
| iso-octane | 10.45 | | | | |

Table 3. Heats of adsorption of alkanes on some oxidic surfaces. [a] this work; [b] KISELEV [15]; [c] different Authors (from YOUNG and CROWELL [16]).

## Discussion

At very low surface coverages, if it is assumed that Henry's adsorption law holds [2], we have

$$p = c_H \vartheta \tag{1}$$

where $p$ = equilibrium partial pressure of adsorbate; $\vartheta$ = surface coverage; $c_H$ = Henry's law constant. The standard chemical potential difference, which can be expressed [8] as

$$\mu_g^0 - \mu_a^0 = k\,T \ln \frac{N_s \vartheta}{p(1-\vartheta)}\,, \tag{2}$$

in these particular conditions can be written

$$\mu_g^0 - \mu_a^0 = k\,T \ln (N_s \vartheta / p) \tag{3}$$

where $N_s$ = total number of adsorption sites. Further, in terms of statistical thermodynamics, the same difference can be expressed by

$$\mu_g^0 - \mu_a^0 = -k\,T \ln[(2\,\pi\,m\,k\,T)^{3/2}\,k\,T\,f_i/h^3] + u_g + k\,T \ln f_i\,f_s\,N_s - u_a \tag{4}$$

where $f_i$, $f_s$ = partition functions resp. for the internal motions and for "such motions (translation, vibration, etc.) as the molecules may execute on the surface" [8]; $u_g$, $u_a$ = average potential energy of the gaseous and of the adsorbed molecules; $m$ = mass of a molecule.

By equating Eqs. (3) and (4), taking into account Eq. (1), differentiating with respect to $T$, and multiplying by $T$, we obtain

$$-u_g + u_a - \tfrac{5}{2}\,k\,T + \varepsilon_s = -k\,T^2 \left(\frac{\mathrm{d} \ln c_H}{\mathrm{d}T}\right)_{N_s} = -\lambda \tag{5}$$

where $\varepsilon_s$ = average energy of a molecule due to motion in the surface; $\lambda$ = heat of adsorption per molecule. On passing to molar quantities and putting

$$N(u_g - u_a) = U_g - U_a = P_{ads}\,,$$

and

$$N\,\varepsilon_s = E_s = 2 \cdot \tfrac{1}{2}\,R\,T + E_{a,v}$$

(where $P_{ads}$ = molar potential energy of adsorption; $E_{a,v}$ = molar energy for a vibration perpendicular to the surface [9]), we have Eq. (6) which is similar to that proposed by Ross and OLIVIER [10]:

$$Q_a = P_{ads} + \tfrac{3}{2}\,R\,T - E_{a,v}\,. \tag{6}$$

For a series of homologous compounds, Eq. (6) demands a linear relation between $Q_a$ and $P_{ads}$, at constant $T$ (and practically in a narrow temperature range as here employed), if also $E_{a,v}$ is constant for that series. It can be easily shown [11] that this might be the case with n-alkanes.

The dependence of $P_{ads}$ on the number of C atoms, $n_C$, can be foreseen by assuming that with a group $i$, such as methyl or methylene, dispersion forces only are effective. Taking into account the interaction of the adsorbed group with the surface atoms only, we have [12]:

$$P_{ads,\,i} = P_{disp,\,i} = \tfrac{3}{10}\,\pi\,\varrho\,r_e^{-4}\,C_{KM} + \ldots \tag{7}$$

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[8] E. A. MOELWIN-HUGUES, Physical Chemistry, Pergamon Press, London 1957, p. 929–930.

[9] The expression given for $E_s$ implies the well known bidimensional gas model, in which the adsorbed molecules have lost one translational degree of freedom, relative to the gas, and acquired a new vibrational degree in a direction normal to the surface, with the additional assumption that changes in rotational degrees are not much significant. As to Eq. (5), it can be also recognised that it is the term at the right giving the possibility of determining adsorption heats by GSC (S. ROSS, J. K. SAELENS, and J. P. OLIVIER, J. Phys. Chem. **66**, 696 [1962]). Further, it can be shown that at the limit for $\vartheta \rightarrow 0$ the gas-chromatographic and the isosteric heats of adsorption coincide.

[10] See ref. [1], pp. 234, 238.

[11] If molecules are adsorbed in a "lying-down" position (S. E. HOORY and J. M. PRAUSNITZ, Trans. Faraday Soc. **63**, 455 [1967]), the equilibrium distance $r_e$ can be assumed to be constant for all groups in a n-alkane molecule and also from one homologue to another. Further, if the perpendicular vibration frequency $\nu$ is proportional to $(P_{ads}/M)^{\frac{1}{2}}\,r_e^{-1}$, where $M$ = mol. weight (see S. ROSS [1], p. 268), we can write by an acceptable approximation

$$\nu \propto (n_C\,P_{ads,\,CH_2}/n_C\,M_{CH_2})^{\frac{1}{2}}\,r_e^{-1}\,,$$

where $n_C$ = number of C atoms, $P_{ads,\,CH_2}$ and $M_{CH_2}$ = adsorption potential and mol. weight for each $CH_2$ group. Thus, $\nu \cong \mathrm{const} \cdot r_e^{-1}$ and $\nu \cong \mathrm{const}$ through a n-alkane series; consequently also $E_{a,v} = N\,h\,\nu / (e^{h\nu/kT} - 1)$ is roughly a constant at $T = \mathrm{const}$.

[12] Ref. [1], p. 265.

where $\varrho$ = specific number of atoms in the solid surface layer, $r_e$ = average equilibrium distance of group $i$ from surface and $C_{KM} \equiv$ Kirkwood-Mueller [13] constant,

$$C_{KM} = (6\, m\, c^2\, \alpha_i) / (\alpha_s/\chi_s + \alpha_i/\chi_i),$$

with $m$ = mass of the electron, $c$ = velocity of light, $\alpha_s$, $\alpha_i$ = electronic polarizability of solid and group $i$, respectively, and $\chi_s$, $\chi_i$ = magnetic susceptibility of the same. Since $\varrho$, $r_e$, $\alpha_s$ and $\chi_s$ are constants, Eq. (7) becomes:

$$P_{ads,\, i} = A\, \alpha_i / (B + \alpha_i/\chi_i), \qquad (8)$$

$A$ and $B$ being constants. It may be seen [14] that $\alpha_i/\chi_i$ for methyl and methylene is also a constant, $C$. Thus

$$P_{ads,\, i} = A\, \alpha_i / (B + C) = D\, \alpha_i\,. \qquad (9)$$

By applying Eq. (9) to each methyl and methylene group of the hydrocarbon chain and by summation, the total adsorption potential can be expressed as

$$P_{ads} = D\, \alpha \qquad (10)$$

where $\alpha$ is the overall electronic polarizability of the hydrocarbon. It can be seen (Fig. 4-A) that the electronic polarizability of alkanes is a strictly linear function of $n_C$; consequently, by comparison of Eqs. (10) and (6), a linear dependance of $Q_a$ on $n_C$ can also be established. The experimental results are in agreement with this statement (Fig. 4-B) and the corresponding equation is

$$Q_a = 2.12 + 1.21\, n_C \quad \text{(kcal/mole)} \qquad (11)$$

where the coefficient 1.21 obviously represents the average increment of the adsorption potential for each $CH_2$ group, in the considered $n_C$ range. When one or more $CH_2$ or $CH_3$ groups are at a greater distance from the surface, it is seen from Eq. (7) that their contribution to the total adsorption potential should be strongly diminished, even if the electronic polarizability were the same. This is confirmed by the experimental data for n-octane and iso-octane (Table 3).

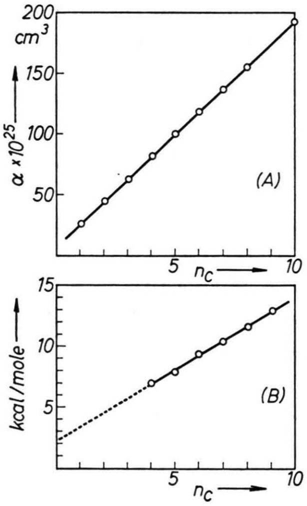

Fig. 4. A) : electronic polarizability of alkanes and B) : heat of adsorption (at zero coverage) of n-alkanes, as functions of the carbon atoms number.

For comparison, in Table 3 the heats of adsorption obtained by other authors for some n-alkanes on other oxidic surfaces are given. Since the small differences relative to $\gamma$-$Al_2O_3$ (as an average 5.7% for $SiO_2$ and 3.7% for MgO) might in part be due to the different experimental conditions, it is apparent that in the above systems the same type of interaction is involved.

On the other hand, it has been shown by theoretical calculations [15, 16] that with $SiO_2$-gel and MgO the contribution of electrostatic interaction with the crystal surface field is negligibly small. Our assumption in deriving the linear relation (10) by simply applying the dispersion potential (7), seems therefore to be remarkably supported. The absence of outstanding phenomena due to strongly charged surface cationic vacancies (as supposed in oxides of 1 : 2 and 2 : 3 types, such as $SiO_2$ and $Al_2O_3$, but not for 1 : 1 type as MgO [17, 18]) is quite remarkable. Similarly, a striking feature of the above systems is also the lack of specific interactions with cations of different polarizing power as $Mg^{2+}$, $Al^{3+}$ and $Si^{4+}$.

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[13] D. H. Young and A. D. Crowell, Physical Adsorption of Gases, Butterworth Sci. Publ., London 1962, p. 9.

[14] From reported data (Landolt-Börnstein, Zahlenwerte und Funktionen, VI. Aufl., I. Band, 3. Teil, Springer-Verlag, Berlin 1951) it can be seen that a linear relation exists between $\alpha$ and $\chi$ for the n-alkanes, i. e., $\alpha = C\,\chi$. Assuming additivity for both properties, the equation may be written

$$2\,\alpha_{CH_3} + (n_C - 2)\,\alpha_{CH_2} = 2\,C\,\chi_{CH_3} + (n_C - 2)\,C\,\chi_{CH_2}$$

which can be solved putting $\alpha_{CH_3}/\chi_{CH_3} = \alpha_{CH_2}/\chi_{CH_2} = C$.

[15] A. V. Kiselev, Proc. 2nd Intern. Congr. Surface Activity, Butterworths Sci. Publ., London 1957, p. 179.

[16] Ref. [13], p. 45.

[17] J. B. Peri, J. Phys. Chem. **69**, 220 [1965].

[18] J. King Jr. and S. W. Benson, J. Chem. Phys. **44**, 1007 [1966].