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DETERMINATION OF ADSORPTION ENTHALPIES AND ENTROPIES OF INORGANIC HALIDES BY TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHY

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SUMMARY

The possibilities of using temperature-programmed gas–solid chromatography for the determination of adsorption enthalpies and entropies of inorganic chlorides are investigated. This method is suitable, if data of limited accuracy are acceptable, whereas for more precise data isothermal gas chromatography is recommended. The advantage of temperature-programmed experiments is that simultaneous investigations can be made of compounds with very different volatilities. The results of these investigations support the picture of "surface complexes" between the adsorbed molecules (metal halides or oxyhalides, *e.g.*, $ReCl_5$, $SnCl_4$, $PoCl_4$, etc.) and the adsorbent (alkali metal halides, SiO_2).

INTRODUCTION

In a recent paper[1] we presented the possibility of determining adsorption data of inorganic halides (*e.g.*, $ZrCl_4$, $NbCl_5$, etc.) on solid surfaces (*e.g.*, ionic halides, graphite) by means of isothermal gas chromatography (GC) and gave the results of an extensive investigation with this method. In the present paper the possibilities of using temperature-programmed GC for the determination of adsorption enthalpies and entropies are described and the results of these investigations are presented. The advantage of temperature-programmed experiments is that a large number of compounds with very different adsorption properties can be investigated within a single series of experiments. This is not possible in isothermal GC because at high temperatures compounds of high volatility would be eluted together with the air peak, and at low temperatures compounds of low volatility would not be eluted within a reasonable time. Therefore in isothermal investigations it is necessary to adjust the temperature range of the investigation according to the volatility of a compound or group of compounds. The advantages and disadvantages of both methods will be discussed in more detail later in this paper.

THEORETICAL

In another paper[1] it has been shown that in inorganic gas adsorption chromatography the migration of a substance can be described by

$$\frac{dx}{dt} = \frac{\vec{u}\,(T)}{1 + \dfrac{a_0 \cdot F}{P_0 \cdot V_0}\,e^{-\Delta H^0/RT} \cdot e^{\Delta S^0/R} \cdot R \cdot T}$$

(1)

where:

a_0 = standard surface concentration
F = surface of the stationary phase
P_0 = standard pressure
V_0 = free column volume
$\vec{u}\,(T)$ = linear gas velocity at temperature T
$\dfrac{dx}{dt}$ = migration velocity of the substance
ΔH^0 = standard adsorption enthalpy
ΔS^0 = standard adsorption entropy

If T is a function of the time, $T = T(t)$, the integral equations:

$$l = \int_{t_0}^{t} \frac{\vec{u}\,(T(t))}{1 + \dfrac{a_0 \cdot F \cdot R \cdot T(t)}{P_0 \cdot V_0} \cdot e^{-\Delta H^0/RT(t)} \cdot e^{\Delta S/R}}\, dt$$

(2)

where:

t_0 = starting time of the chromatographic experiment
l = position of the substance at time t

or

$$t - t_0 = \int_{0}^{l} \left(\frac{1}{\vec{u}\,(T(t))} + \frac{a_0 \cdot F \cdot R \cdot T(t)}{P_0 \cdot V_0 \cdot \vec{u}\,(T(t))} \cdot e^{-\Delta H^0/RT(t)} \cdot e^{\Delta S^0/R} \right) dx$$

(3)

cannot be solved in a closed form. These equations can either be solved by numerical methods (standard programs for this kind of mathematical problem are available for most of the common programming languages) or with the help of approximations. Giddings[2] has suggested a very good and useful approximation for linear temperature-programmed GC ($T = T_0 + at$). The condition for this approximation $\Delta H^0/RT > 2$, is true for practically all realistic problems. With this approximation eqn. 2 can be solved and the following expression is obtained:

$$\frac{R \cdot T_R \cdot F \cdot a_0 \cdot l \cdot a \cdot e^{\Delta S^0/R}}{V_0 \cdot P_0 \cdot \vec{u}_{T_R} \cdot \Delta H^0/R} = \frac{e^{-\Delta H^0/RT_0}}{\left(1 + \dfrac{\Delta H^0}{RT_0}\right)^2} - \frac{e^{-\Delta H^0/RT}}{\left(1 + \dfrac{\Delta H^0}{RT}\right)^2}$$

(4)

(u_{T_R} is the linear gas velocity at room temperature T_R; l is the position of the substance at the time the column has reached temperature T; if T is the elution temperature, l is identical to the total column length L, but in principle eqn. 4 describes the position of the substance at any temperature T.)
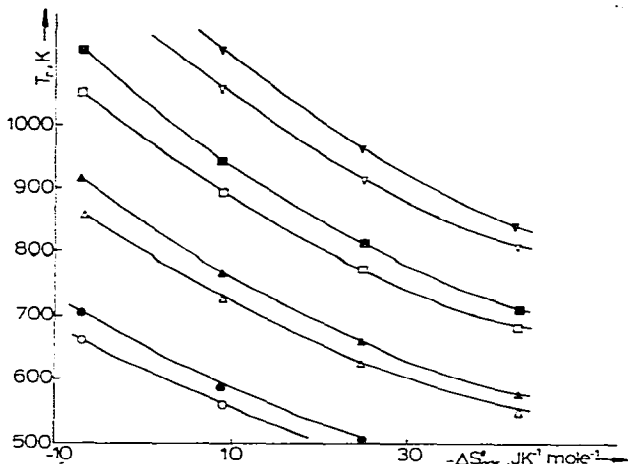
Fig. 1. Comparison of retention temperatures (T_r) calculated from eqn. 3 (numerical integration, solid lines) and from eqn. 4; $\bigcirc$, $\bullet$, $H^0_{ads} = -50$ kJ mole^{-1}; $\triangle$, $\blacktriangle$, $H^0_{ads} = -66.4$ kJ mole^{-1}; $\square$, $\blacksquare$, $H^0_{ads} = -83$ kJ mole^{-1}; $\bigtriangledown$, $\blacktriangledown$, $H^0_{ads} = -100$ kJ mole^{-1}; $\bigcirc$, $\triangle$, $\square$, $\bigtriangledown$, $a/\vec{u}_{T_R} = 1$ °K cm^{-3}; $\bullet$ $\blacktriangle$, $\blacksquare$, $\blacktriangledown$, $a/\vec{u}_{T_R} = 2$ °K cm^{-3}. $a_0 = 1.37 \cdot 10^{-11}$ mole cm^{-2}; $P_0 = 1$ atm; $l = 75$ cm; $F = 6 \cdot 10^3$ cm^2; $V_0 = 19$ cm^3.

A comparison between values obtained from this solution and values calculated by numerical integration of eqn. 3 demonstrates that eqn. 4 is valid for the practical problems in temperature-programmed inorganic gas adsorption chromatography (Fig. 1).

Unfortunately eqn. 4 cannot be solved or rearranged to give an explicit expression for the dependence of T from the adsorption enthalpy and entropy. The general problem which has to be solved in order to determine adsorption enthalpies and entropies from the results of temperature-programmed GC is to find the ΔH^0 and ΔS^0 values which best fit the measured dependence of the retention temperature T from the experimental parameters (see for example Fig. 2). Whether this is done by
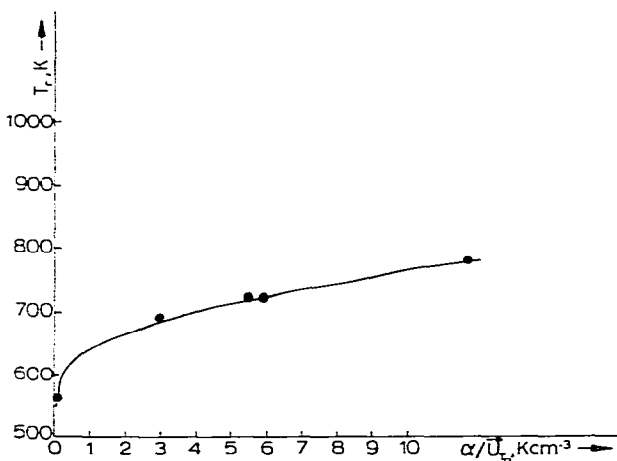

Fig. 2. Retention temperatures as function of $a/\vec{u}_{T_R}$ for ReOCl$_3$ on quartz glass surface. $\bullet$, Experimental values: ——, calculated for $\Delta H^0_{ads} = -99$ kJ mole^{-1}, $\Delta S^0_{ads} = -74$ JK^{-1} mole^{-1}.

numerical or graphical methods, it is time-consuming and tedious. A better way of finding the proper ΔH^0 and ΔS^0 values is as follows. For a retention temperature determined for a given set of experimental parameters (a, l, $\vec{u}_{T_R}$, V_0, F) the dependence of ΔS^0 on ΔH^0 can be calculated with the help of eqn. 4. If this is done for the same compound and kind of surface, but for two or more sets of different experimental parameters (and therefore for different retention temperatures), the ΔH^0_{ads} values for this adsorpent–adsorbate pair are simply the points of intercept of the different $\Delta H^0 / \Delta S^0$ curves (see Fig. 3).
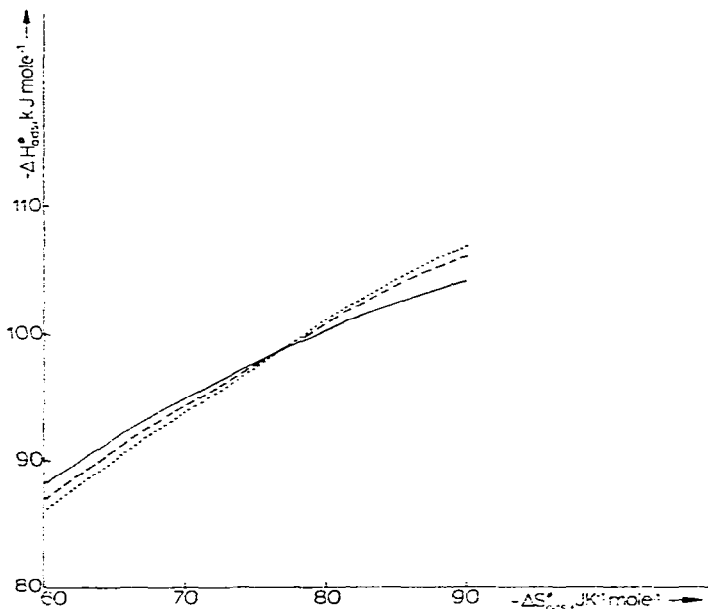

Fig. 3. Determination of adsorption enthalpies and entropies from retention temperatures (same example as Fig. 2). ——, $T_r = 565\ °K$, $a/\vec{u}_{T_R} = 0.1$; – – – –, $T = 690\ °K$, $a/\vec{u}_{T_R} = 3$; · · · ·, $T_r = 780\ °K$, $a/\vec{u}_{T_R} = 11.7$.

If more than two different curves are used, there is usually more than one point of intercept, due to the experimental errors. But for sufficiently exact data, the region of ΔS^0 and ΔH^0 in which these points are found is small, so that no difficulties arise in the determination of average adsorption enthalpies and entropies. In order to check the agreement with the experimental value, we calculated the retention temperatures by numerical integration of eqn. 3 and compared these temperature values with the results of the experimental retention temperature measurements. It should be mentioned that, although eqn. 4 is a very good approximation for eqn. 3, the use of eqn. 3 has some advantages for practical purposes although the numerical integration requires an increased effort. In temperature-programmed GC it is very difficult to achieve an absolutely temperature-independent gas flow-rate, therefore $\vec{u}_{T_R}$ is usually a function of the temperature (or time). This can be taken into consideration if the temperature gas-flow dependence is measured, and eqn. 3 integrated with $\vec{u}_{T_R}$ as a function of temperature. We have found that eqn. 4 may be used with the $\vec{u}_{T_R}$ value at the retention temperature, if the change of the flow-rate is less than 1 % for a temperature

change of 10 °K. In this case the error caused by this simplification is small compared with the experimental errors.

EXPERIMENTAL

The equipment has been described in detail[3]. Only the special experimental conditions will be mentioned. Chromatographic column: effective length 75 cm, I.D. 8 mm, O.D. 10 mm; particle size of packing, 0.16–0.315 mm, kind of packing, graphite, quartz glass, quartz glass coated with NaCl or CsCl; free column volume 19 cm^3; surface of solid phase 6 · 10^3 cm^3. Carrier gas: nitrogen with a CCl$_4$ partial pressure of 90 mmHg; flow-rate at room temperature, 0.8–350 cm^3 min^{-1}. Linear temperature program: $T = T_0 + at$, $T_0 = 300$ °K, $a = 2$–24.5 °K min^{-1}, maximum final temperature 1100 °K.

RESULTS AND DISCUSSION

In order to test whether eqns. 3 and 4 agree with the experimental results and if their use is justified in realistic experiments, we made a number of measurements for combinations of stationary phases and volatile compounds, for which the adsorption enthalpies and entropies had already been determined by isothermal GC[1]. In Fig. 4 experimental retention temperatures (points) are compared with retention data calculated from known adsorption data (solid lines). The results clearly indicate that eqns. 3 and 4 present the correct dependence of the retention temperature from the experimental parameters and the adsorption enthalpy and entropy. Consequently, the method outlined in Theoretical should give results which are correct within purely experimental errors.

Table I lists adsorption enthalpies and entropies which have been determined by the use of temperature-programmed GC. The average errors are 10–20 kJ mole^{-1} for ΔH_{ads} and 15–25 J °K^{-1} mole^{-1} for ΔS_{ads}. The main error source is the experimental error of the retention temperature. From Fig. 5 it is apparent that a relatively small error of the retention temperatures may cause a large error of the adsorption data. Since the angle of intercept of the different $\Delta H^0/\Delta S^0$ curves depends strongly on the difference of the values for the experimental parameters (in our experiments we varied only the gas flow-rate and the heating rate, because these two parameters are easy to control and can be measured very exactly), it is important that the experiments cover a wide range of these parameters. If a larger number of measurements has been used for the determination of the adsorption enthalpies and entropies, the actual errors are probably smaller than mentioned above, but if the adsorption data are calculated from only two or three retention temperatures, very high errors are posisible In this case not only the errors of the retention data have to be taken into account, but another possible error source has to be considered. Thus if a compound decomposes at high temperatures it may behave normally at lower temperatures, but under experimental conditions where the compound would be eluted at higher temperatures, thermal decomposition may be nearly complete and the observed retention temperature should be assigned to the decomposition product of this compound. If this effect is not discovered, results which have very large errors may be obtained. In order to
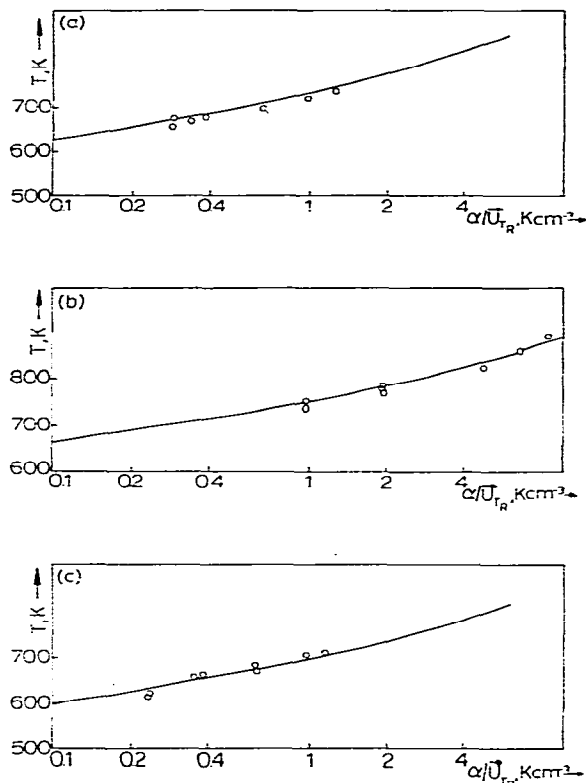
Fig. 4. Comparison of experimental retention temperatures with values calculated from known adsorption enthalpies and entropies: a, $NbCl_5$ on $NaCl$, $\Delta H^0_{ads} = -76$ kJ mole^{-1}, $\Delta S^0_{ads} = -22$ JK^{-1} mole^{-1}; b, $NbCl_5$ on KCl, $\Delta H^0_{ads} = -101$ kJ mole^{-1}, $\Delta S^0_{ads} = -52$ J $^\circ$K^{-1} mole^{-1}; c, $TeCl_4$ on $NaCl$, $\Delta H^0_{ads} = -70$ kJ mole^{-1}, $\Delta S^0_{ads} = -18$ J $^\circ$K^{-1} mole^{-1}.

judge the reliability of the data in Table I, the number of measurements from which the data are derived is also included.

The errors for data determined by temperature-programmed GC are considerably larger than for data from isothermal GC. The advantage of temperature-programmed experiments is that a large number of compounds with very different volatilities can be investigated simultaneously. The purpose of this investigation was to determine the adsorption enthalpies of chlorides and oxychlorides of a large number of different elements for various surfaces. This is a valuable extension of our previous study of the adsorption properties of different chlorides and oxychlorides of five elements (Nb, Zr, Yc, Te, Mo) on various surfaces. This study indicated that the compounds under investigation formed donor–acceptor complexes with the surfaces which might be called "surface complexes". These complexes show analogies with the corresponding chloride complexes in the bulk phase, as with the gas-phase halide complexes. The results obtained from temperature-programmed investigations agree with these assumptions, and some especially interesting points will be mentioned.

(1) The pentachlorides of the second and third row of the transition elements have very similar adsorption properties, whereas the pentachlorides of several other elements show very different properties (Table II). These can be expected from the

TABLE I

ADSORPTION ENTHALPIES AND ENTROPIES DETERMINED BY THE USE OF TEMPERATURE PROGRAMMED GAS CHROMATOGRAPHY

Compound*	Surface	ΔH^0_{ads} (kJ mole^{-1})	ΔS^0_{ads} (JK^{-1} mole^{-1})	No. of points of measurement
ReOCl$_3$	SiO2	-99	-74	4
TaCl$_5$	SiO$_2$	-66	-4	3
(TaOCl$_3$)	SiO$_2$	-133	-70	3
TlCl$_3$	SiO$_2$	-59	-5	2
TlCl	SiO$_2$	-130	-73	2
GaCl$_3$	SiO$_2$	-58	1	2
CdCl$_2$	SiO$_2$	-65	0	3
PbCl$_2$	SiO$_2$	-125	-42	2
InCl$_3$	SiO$_2$	-103	-66	3
InCl	SiO$_2$	-142	-87	5
SnCl$_4$	SiO$_2$	-54	-32	5
SnCl$_2$	SiO$_2$	-106	-83	5
PoCl$_4$	SiO$_2$	-69	-11	5
PoCl$_2$	SiO$_2$	-133	-74	4
BiCl$_3$	SiO$_2$	-101	-53	5
Bi	SiO$_2$	-132	-65	7
SbCl$_5$	SiO$_2$	-34	14	4
SbCl$_3$	SiO$_2$	-69	-22	3
ICl	SiO$_2$	-25	28	8
ReCl$_5$	NaCl	-64	-7	5
ReCl$_6$	NaCl	-31	39	2
SnCl$_4$	NaCl	-29	38	5
SnCl$_2$	NaCl	-42	26	3
TlCl$_3$	NaCl	-55	17	2
TlCl	NaCl	-70	11	2
ICl	NaCl	-32	35	5
BiCl$_3$	NaCl	-86	-24	4
Bi	NaCl	-75	-25	3
PoCl$_4$	NaCl	-88	-43	3
PaCl$_5$	NaCl	-126	-53	5
SbCl$_5$	NaCl	-36	25	5
TaOCl$_3$	NaCl	-96	-23	3
HfCl$_4$	NaCl	-99	-26	3
ZrCl$_4$	NaCl	-99	-26	3
GaCl$_3$	NaCl	-38	18	2
OsCl$_4$	NaCl	-101	-7	3
InCl$_3$	NaCl	-67	18	2
PaCl$_5$	CsCl	-126	-53	2
HfCl$_4$	CsCl	-104	-26	2
InCl$_3$	CsCl	-71	$-i$	2
InCl	CsCl	-138	-66	3
SnCl$_4$	CsCl	-31	35	3
ICl	CsCl	-34	26	4
SbCl$_5$	CsCl	-39	14	3

* The stated compounds are the most probably formed species; if the assignment is not completely justified, the compound is enclosed in parentheses. If there is insufficient evidence as to the dentity of the compound, only the element is stated.
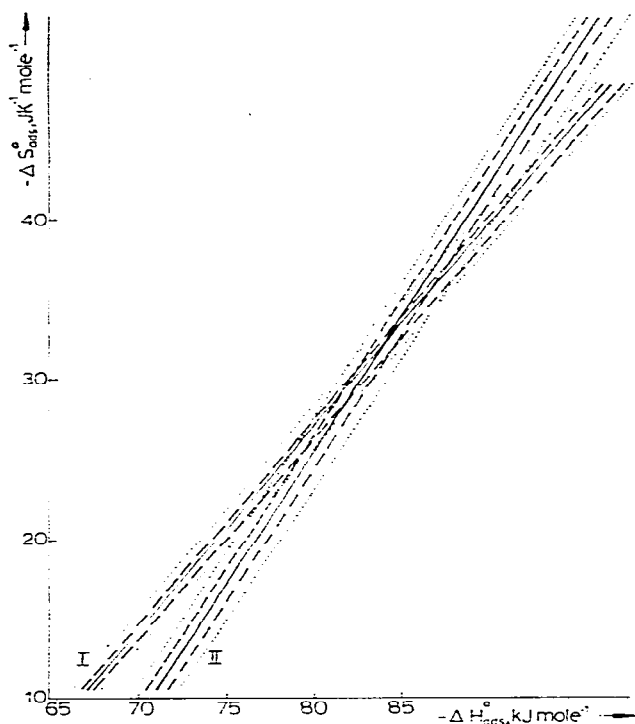
Fig. 5. Demonstration of the influence of the errors of retention temperatures on the errors of the adsorption enthalpies and entropies for $NbCl_5$ on $CaCl_2$ surface: I, $a/\vec{u}_{T_R} = 10$. $T_r = 848\ °K$; II, $a/\vec{u}_{T_R} = 0.1$, $T_r = 633\ °K$. ——, T_r; – – – –, $T_r \pm 5\ °K$; . . . ., $T_r \pm 10$ K.

known chemical properties of these elements. Thus, the transition-mental pentachlorides of the third and second row form quite similar halide complexes, but the properties of the main-group and actinide pentahalides are very different. Similar

TABLE II

ADSORPTION DATA OF DIFFERENT PENTACHLORIDES

Compound	Surface	ΔH^0_{ads} (kJ mole^{-1})	ΔS^0_{ads} (JK^{-1} mole^{-1})
$NbCl_5$[*]	NaCl	-76	-22
$TaCl_5$	NaCl	-96	-23
$MoCl_5$[*]	NaCl	-72	-12
$ReCl_5$	NaCl	-64	-7
$SbCl_5$	NaCl	-36	25
$PaCl_5$	NaCl	-126	-53
$NbCl_5$[*]	SiO_2	-65	-11
$TaCl_5$	SiO_2	-66	-4
$MoCl_5$[*]	SiO_2	-57	-10
$SbCl_5$	SiO_2	-34	14
$NbCl_5$[*]	CsCl	-86	-44
$MoCl_5$[*]	CsCl	-76	-27
$PaCl_5$	CsCl	-126	-53
$SbCl_5$	CsCl	-39	14

[*] Data from ref. 3.

TABLE III

ADSORPTION DATA OF DIFFERENT TETRACHLORIDES

Compound	Surface	ΔH^0_{ads} (kJ mole^{-1})	ΔS^0_{ads} (JK^{-1} mole^{-1})
ZrCl$_4$[*]	SiO$_2$	-97	-54
TcCl$_4$[*]	SiO$_2$	-85	-15
SnCl$_4$	SiO$_2$	-54	-32
PoCl$_4$	SiO$_2$	-69	-11
TeCl$_4$[*]	SiO$_2$	-57	-7
ZrCl$_4$	NaCl	-99	-26
OsCl$_4$	NaCl	-101	-7
HfCl$_4$	NaCl	-99	-26
TeCl$_4$[*]	NaCl	-70	-8
PoCl$_4$	NaCl	-88	-43
SnCl$_4$	NaCl	-29	38
HfCl$_4$	CsCl	-104	-26
TcCl$_4$[*]	CsCl	-75	10
TeCl$_4$[*]	CsCl	-42	10
SnCl$_4$	CsCl	-31	35

[*] Data from ref. 3.

examples exist also for other types of compounds (*e.g.*, ZrCl$_4$, HfCl$_4$, ReCl$_4$ and TcCl$_4$ have properties quife different from TeCl$_4$ or SnCl$_4$, Table III).

(2) The adsorption enthalpies and enthalpies for the formation of chloride complexes show interesting parallels (Table IV). It is not surprising that the complexes in the bulk phases have lower enthalpies than the surface complexes (*ca.* 10 kJ mole^{-1}).

(3) The experimental data show a correlation between adsorption enthalpies and entropies which is very similar to the dependence which has been observed for the adsorption data of Tc, Te, Nb, Mo and Zr halides. This phenomenon has already been discussed in more detail[1].

Although up to now there has been no direct information about the structures of the different surface complexes, we think that the various adsorption data determined by temperature-programmed GC present further evidence for the following simplified picture of the chemisorbed state of the investigated type of adsorbent–adsorbate systems.

(1) The interaction between the chemisorbed molecule and the surface is in principle a Lewis acid–base interaction.

TABLE IV

COMPARISON OF ENTHALPIES OF ADSORPTION AND OF COMPLEX FORMATION

Surface	Compound	ΔH^0_{ads} (kJ mole^{-1})	$\Delta H^0_{compl.}$ (kJ mole^{-1}) [*]
NaCl	NbCl$_5$[**]	-76	-91
KCl	NbCl$_5$[**]	-101	-112
NaCl	TaCl$_5$	-96	-115
NaCl	ZrCl$_4$	-99	-108
NaCl	HfCl$_4$	-99	-109

[*] Data from ref. 4.
[**] Data from ref. 3.

(2) This reaction is the main kind of interaction between surface and adsorbed molecule. Van der Waals forces and similar purely physical influences may take part in the adsorbent–adsorbate interaction, but cannot explain the observed adsorption enthalpies.

(3) The chemisorbed molecules act as Lewis acids.

(4) The surface adsorption sites act as Lewis bases.

(5) Towards an adsorbed molecule, surface sites may act as mono- or polydentate ligands, depending on the chemisorbed molecule and possibly on the special surface site. (There is at the moment no evidence as to whether a single surface site may act both as a mono- and as a polydentate ligand, or if a definite surface site represents either a mono- or a polydentate ligand.)

(6) The adsorbed molecules have limited degrees of freedom (rotational and vibrational degrees of freedom, perhaps the possibility of a restricted "hopping" movement from surface site to surface site).

(7) The hindrance of the rotational, vibrational and translational movements depends on the strength of the chemisorptive bond.

CONCLUSIONS

The method of temperature-programmed gas chromatography enables the determination of adsorption data for a large number of compounds of different volatility within a limited number of experiments. The results have larger errors than data from isothermal investigations, but the results of both variants are identical within the margins of error. The use of temperature-programmed GC for the determination of adsorption data is recommended if a simple and short overview over a wide range of different compounds is desired, and if extreme precision of the obtained data is not essential.

The data obtained by this method can be interpreted by the outlined picture of surface complex formation. The wide scope of the presented data indictes that surface complex formation may be general for the interaction between gaseous compounds with strong Lewis-acid character and surfaces of solid compounds with Lewis-base character. In our opinion surface complexes may be "intermediate" in chemical nature between the solid- and the gas-phase complexes.

Besides further detailed experimental investigations and efforts to develop more refined (if possible quantitative) theories based on these data, two points should receive special attention.

(1) Interaction of volatile inorganic Lewis bases with solid compounds of Lewis-acid character (this presents considerable difficulties, since it is extremely hard to find combinations of this kind).

(2) Substitution reactions with surface complex of the kind

$$AX_{n(gas\ phase)} + BX_{m(chemisorbed)} \rightarrow BX_{m(gas\ phase)} + AX_{n(chemisorbed)}$$
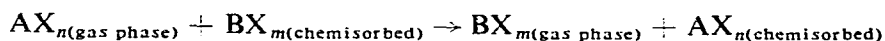
(In systems of this type it may sometimes be difficult to determine to which reaction (or reaction chain) the measured data should be assigned.) The results of experiments of this kind would present further evidence about the nature of the described surface complexes. If our conclusions about the observed gas–solid interaction are justified,

inorganic surface complexes may be of similar scientific interest as the well known inorganic gas-phase complexes and it is to be hoped that understanding of the chemical interactions in inorganic gas-phase, solid and surface complexes can be further improved by comparisons of all three complex types.

ACKNOWLEDGEMENTS

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