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USE OF ISOTHERMAL GAS CHROMATOGRAPHY FOR THE DETERMINATION OF THE ADSORPTION ENTHALPIES AND ENTROPIES OF INORGANIC HALIDES AT HIGH TEMPERATURES

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SUMMARY

Gas chromatography was used to determine the adsorption enthalpies and entropies of inorganic chlorides on solid non-porous adsorbents (silica, alkali metal chlorides, graphite, etc.) at high temperatures (650–1100°K). The results demonstrate that gas chromatography is also a useful method for investigations in the field of inorganic chemistry. The adsorption enthalpies and entropies (or rather, chemisorption enthalpies and entropies) indicate that the adsorption (or chemisorption process) involves complex formation between the adsorbed molecules and the adsorbent (coordinative by bonded surface complex).

INTRODUCTION

In recent years various types of gas–solid chromatography for application to inorganic compounds have been developed. The techniques applied include isothermal and temperature-programmed gas chromatography¹, and thermochromatography² and on-line separations or continuous retention time measurements³. The aims of the investigation of the different methods of inorganic gas chromatography are different:

- (1) the development of separation methods for trace elements;
- (2) the determination of thermodynamic data, especially adsorption enthalpies and entropies^{4,5};
- (3) the separation of new artificial elements and the investigation of the chemical properties of these elements and their compounds⁶.

In an extensive study, we have investigated the chromatographic behaviour of various metal chlorides and oxychlorides in columns with different solid inorganic stationary phases. An important part of this study was the determination of adsorption enthalpies and entropies by isothermal gas–solid chromatography. In this paper we present the arguments and theory for the calculation of these values from experimental data and the results of the investigations.

THEORETICAL

Most of the investigations were carried out at extremely low surface concentrations and with non-porous solid stationary phases. As such low concentrations were used, it is justified to assume that the adsorption isotherms are linear and therefore that the partition ratio is independent of concentration. For these nearly ideal conditions (non-porous solid stationary phase, linear adsorption isotherm), the migration velocity ($dx/dt = v$) of the first statistical moment of the chromatographic peaks (or the peak maximum of a symmetrical peak) can be expressed by

$$\frac{dx}{dt} = v = \frac{u}{1+k} \quad (1)$$

where u = linear velocity of the carrier gas.

The partition coefficient (or retardation ratio), k , can be expressed as

$$k = \frac{as}{c_g V_g} = K_a \cdot \frac{s}{V_g} \quad (2)$$

where $K_a = a/c_g$ (cm), a = surface concentration, s = surface area, V_g = free column volume and c_g = concentration in the gas phase.

To convert the gas-phase concentration into the partial pressure (p), as a first approximation an ideal gas is assumed:

$$k = \frac{asRT}{lpV_g} = K_p \cdot \frac{sRT}{V_g} \quad (3)$$

where $K_p = a/p$ (mol N⁻¹).

In principle, the adsorption enthalpy can be determined from the temperature dependence of the partial pressure p in the gas phase at constant surface pressure π :

$$\Delta H_{ads} = -RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_{\pi} \quad (4)$$

Theoretically, the adsorption enthalpy can be determined from retention data by combining eqn. 1 (in the integrated form) for constant experimental conditions [$t_r^0 = t_0 \cdot (1+k)$] with eqns. 3 and 4:

$$- \left\{ \frac{\partial \ln \left[\frac{asRT}{V_g (t_r/t_0)} \right]}{\partial T} \right\}_{\pi} RT^2 = \Delta H_{ads} \quad (5)$$

where (t_r^0 = total retention time, t_0 = dead time and $t_r = t_r^0 - t_0$ = net retention time)

The correlation between $(\partial \ln p / \partial T)_{\pi}$ and $(\partial \ln p / \partial T)_{\theta}$ and the following expression, which was derived by Hill⁷:

$$\Delta H_{ads} = -RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_{\theta} + T a \left(\frac{\partial \pi}{\partial T} \right)_{\theta} \quad (6)$$

where θ = relative surface coverage, may be used. The term $RT^2 (\partial \ln p / \partial T)_{\theta} = q_{is}$ is often called the isosteric heat of adsorption.

For the borderline cases of the adsorbed state (totally unhindered movement of the molecules along the surface and completely fixed molecules), the following two equations are obtained:

(1) for immobile adsorbed molecules at low surface concentration:

$$\Delta H_{ads}^f = -R \left[\frac{d \ln\left(\frac{t_r}{t_0 T}\right)}{d\left(\frac{1}{T}\right)} \right] = -R \left[\frac{d \ln\left(\frac{V_r}{TV_g}\right)}{d\left(\frac{1}{T}\right)} \right] \quad (7)$$

where V_r = net retention volume, and

(2) for an ideal two-dimensional gas:

$$\Delta H_{ads}^m = -R \left[\frac{d \ln\left(\frac{t_r}{t_0}\right)}{d\left(\frac{1}{T}\right)} \right] = -R \left[\frac{d \ln\left(\frac{V_r}{V_g}\right)}{d\left(\frac{1}{T}\right)} \right] \quad (8)$$

As the net retention time, t_r , and the net retention volume, V_r , are independent of the surface concentration provided that the adsorption isotherms are linear, the adsorption enthalpies do not depend on the surface concentration and in this instance it is no longer necessary to use partial differentials.

According to eqns. 7 and 8, the adsorption enthalpies can be determined from a graph of either the logarithms of the net retention volumes at the column temperature or the logarithms of the quotients of the net retention volumes at the column temperature and the absolute temperature *versus* the inverse of the absolute temperature. It should be noted that both equations were derived by assuming different states of the adsorbed molecules.

An example is presented in Fig. 1 for a range of temperatures. The retention volumes of tellurium tetrachloride were determined in a gas chromatographic column with yttrium trichloride (on quartz-glass particles as the support) as the stationary phase. Fig. 1a shows a plot according to eqn. 7 and Fig. 1b a plot according to eqn. 8. The two adsorption enthalpies determined from these data are $\Delta H_{ads}^f = -73.2 \pm 2.3$ kJ mole⁻¹ and $\Delta H_{ads}^m = -66.0 \pm 2.3$ kJ mole⁻¹, respectively (data are given for a yttrium trichloride column). As $\theta \ll 1$ in all experiments, it is justified to assume that the adsorption isotherms will be linear. The difference between the above two values is 7.2 kJ mole⁻¹, which is as expected in accordance with RT at the average of the experimental temperatures (*ca.* 880°K).

The adsorption enthalpies listed in Table I are based on the assumption of immobile adsorbed molecules, as our results indicate chemisorption of the molecules rather than a purely physical adsorption process. The standard adsorption enthalpies are determined from the intercept of the curve with the $\ln V_r$ axis according to the following equation:

$$\Delta S_{ads}^\circ = \frac{\Delta H_{ads}^\circ}{T} - R \ln\left(\frac{a_s RT}{V_r P_0}\right) \quad (9)$$

where a_s = standard surface concentration and P_0 = standard (gas phase) pressure.

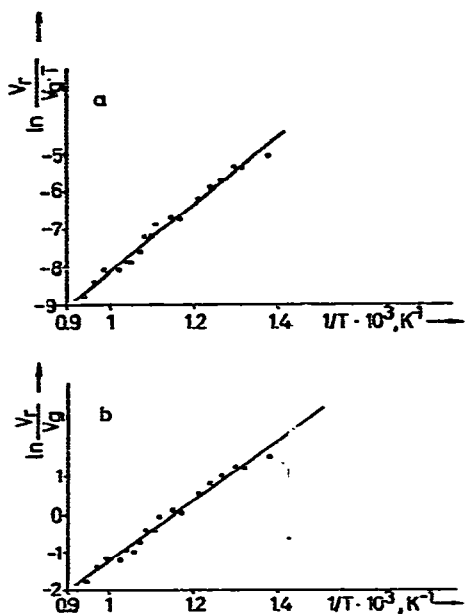


Fig. 1. Arrhenius-type plots for the determination of adsorption enthalpies. (a) Immobile adsorbed molecules; (b) ideal two-dimensional gas. Example: TeCl_4 on a YCl_3 surface.

It can be seen from this equation that the value obtained for the standard adsorption entropy depends on the values used for a_s and P_0 . This is not a problem with P_0 , as a standard pressure of 1 atm is generally used in thermodynamics, but to our knowledge there is no generally accepted standard state for the adsorbed phase. We adopted the standard state suggested by De Boer⁸ for a temperature of 298° K (this gives a value of *ca.* $1.37 \cdot 10^{-11}$ mole cm^{-2}).

EXPERIMENTAL

The experimental procedure and equipment are described in detail elsewhere⁹. The chromatographic section of the column is 75 cm long with an I.D. of 8 mm; the column material was quartz. The columns were packed with quartz-glass or graphite particles or with coated quartz-glass particles of diameter *ca.* 0.25 mm (total surface area = $6 \cdot 10^3$ cm^2). For the investigation, radioactively labelled compounds of high specific activity (carrier free or practically carrier free) were used. Therefore, it was possible to carry out the experiments with extremely small amounts of adsorbate (*ca.* 10^3 molecules cm^{-2}) and the surface coverage, θ , is consequently extremely small ($\theta \ll 1$). The chlorides and oxychlorides were prepared *in situ*, in order to reduce their handling as far as possible. The different radionuclides (Tc-99m, Mo-99, Te-132, Zr-95, Nb-95 and Nb-97) were detected by gamma spectroscopy. The carrier gas was nitrogen with different carbon tetrachloride partial pressures (flow-rate = 1–10 $\text{cm}^3 \text{min}^{-1}$). Carbon tetrachloride was used as a reactive gas for the preparation of volatile chlorides and oxychlorides and was present in the carrier gas to remove oxygen and water impurities as far as possible in order to

prevent the formation of non-volatile oxides and to reduce the thermal dissociation of the investigated compounds into chlorine and compounds of lower oxidation states.

RESULTS AND DISCUSSION

The standard adsorption enthalpies and entropies that were determined by gas-solid chromatography are listed in Table I. Standard states are 1 atm for the gas phase and a surface concentration of $1.37 \cdot 10^{-11}$ mole cm^{-2} for the adsorbed phase. The stated errors are determined from the linear regression of the $\ln V_r/T$ versus T^{-1} plot. The results of identical measurement series are in agreement within the limits of experimental error. The results show that it is justified to neglect the temperature dependence of the adsorption enthalpies and entropies because it is small compared with the experimental errors.

The identification of the chemical compounds presents difficulties in several instances. The measurement method (gamma spectroscopy) permits an unambiguous identification of the element, whereas direct identification of the chemical compounds is not possible. Two sources of information can be used for the identification of the chemical compounds: (1) the known macroscopic properties (*e.g.*, sublimation or evaporation temperatures, enthalpies or entropies); and (2) the chromatographic behaviour and the data derived from the chromatographic properties of the investigated compounds.

The compounds of elements that form only one or two volatile chlorides or oxychlorides can easily be identified from their known macroscopic properties, whereas the compounds of elements that form several different volatile chlorides or oxychlorides (*e.g.*, molybdenum and technetium) can seldom be easily identified. To obtain further evidence about the identity of an unknown compound, it is necessary to compare the observed chromatographic properties with the properties of already identified compounds. By this means it is possible to identify a considerable proportion of the various compounds of different elements, although in some instances the identification is still ambiguous. Several difficulties arise if the macroscopic properties of the chlorides or oxychlorides are not known or are unreliable (*e.g.*, for technetium chlorides or oxychlorides) or if there are no experimental data on the chromatographic properties of similar, already identified compounds.

The high adsorption enthalpies and entropies and the strong dependence of these values on the type of the surface on which the compounds are adsorbed suggest a chemisorption rather than a physisorption process. Both results indicate a selective mutual interaction between adsorbent and adsorbate. The most probable description of this interaction is obtained if coordinative chemical bonding (complex formation) between the surface (electron-pair donor, Lewis base) and the adsorbed molecules (electron-pair acceptor, Lewis acid) is assumed. The experimental data are insufficient in both number and accuracy for any reliable assumptions to be made about the degree of ionic or covalent bonding. For the same reason, it is not possible to make any statements about the contribution of physical forces (repulsion or attraction) to the adsorption enthalpies and entropies. The assumption of the formation of a "surface complex" is supported by the following arguments:

(1) the chlorides and oxychlorides of tellurium, zirconium, niobium, molyb-

TABLE I
ADSORPTION ENTHALPIES AND ENTROPIES

Compound*	Surface	Partial pressure of reactive gas (mmHg)	ΔH_{ads} (kJ mole ⁻¹)	ΔS_{ads} (J mole ⁻¹ °K ⁻¹)	Regression coefficient	Number of points
NbCl ₅	SiO ₂ , 1st series	90 (CCl ₄)	- 69 ± 5	- 20 ± 6	0.9806	9
NbCl ₅	SiO ₂ , 2nd series	90 (CCl ₄)	- 65 ± 5	- 11 ± 5	0.9757	12
NbCl ₅	SiO ₂ , carbon modified	90 (CCl ₄)	- 60 ± 2	- 8 ± 3	0.9912	15
NbCl ₅	Graphite	90 (CCl ₄)	-109 ± 11	- 41 ± 11	0.9581	13
NbCl ₅	Graphite, RuCl ₃ , treated	90 (CCl ₄)	-121 ± 11	- 53 ± 12	0.9502	14
NbCl ₅	SiO ₂	55 (CCl ₄)	- 72 ± 7	- 20 ± 8	0.9710	8
NbCl ₅	SiO ₂	25 (CCl ₄)	- 64 ± 5	- 10 ± 5	0.9783	10
NbCl ₅	SiO ₂	15 (CCl ₄)	- 69 ± 4	- 15 ± 5	0.9825	11
NbOCl ₃	SiO ₂	25 (CCl ₄)/ 15 (H ₂ O)	- 94 ± 13	- 34 ± 14	0.8814	17
NbCl ₅	NaCl	90 (CCl ₄)	- 76 ± 11	- 22 ± 11	0.9372	9
NbCl ₅	MgCl ₂	90 (CCl ₄)	- 76 ± 4	- 23 ± 5	0.9939	7
NbCl ₅	CaCl ₂	90 (CCl ₄)	- 82 ± 3	- 30 ± 4	0.9891	16
NbCl ₅	YCl ₃	90 (CCl ₄)	- 78 ± 4	- 20 ± 5	0.9814	16
NbCl ₅	CsCl heated at 950 °K	90 (CCl ₄)	- 62 ± 3	- 12 ± 4	0.9967	5
NbCl ₅	CsCl heated at 870 °K	90 (CCl ₄)	- 86 ± 4	- 44 ± 6	0.9963	5
NbCl ₅	KCl, 1st series	90 (CCl ₄)	-101 ± 4	- 52 ± 5	0.9968	6
NbCl ₅	KCl, 2nd series	90 (CCl ₄)	-102 ± 4	- 57 ± 5	0.9974	5
NbCl ₅	KCl, HfCl ₄ , heated	90 (CCl ₄)	- 84 ± 8	- 34 ± 10	0.9779	6
NbCl ₅	KCl, RuCl ₃ , heated	90 (CCl ₄)	- 81 ± 8	- 32 ± 9	0.9871	5
Mo	SiO ₂ , 1st series	90 (CCl ₄)	- 75 ± 3	- 30 ± 3	0.9975	5
Mo	SiO ₂ , 1st series	90 (CCl ₄)	-119 ± 10	- 56 ± 21	0.9933	4
(MoOCl ₃)	SiO ₂ , 1st series	90 (CCl ₄)	- 94 ± 8	- 46 ± 9	0.9939	4
MoCl ₅	SiO ₂ , 2nd series	90 (CCl ₄)	- 57 ± 2	- 10 ± 3	0.9952	7
(MoOCl ₃)	SiO ₂ , 2nd series	90 (CCl ₄)	- 81 ± 6	- 31 ± 7	0.9767	10
Mo	SiO ₂ , 2nd series	90 (CCl ₄)	-111 ± 20	- 46 ± 21	0.9696	4
MoCl ₅	SiO ₂ , carbon modified	90 (CCl ₄)	- 46 ± 4	1 ± 4	0.9797	9
(MoOCl ₃)	SiO ₂ , carbon modified	90 (CCl ₄)	- 71 ± 6	- 19 ± 7	0.9868	6
(MoOCl ₃)	Graphite	90 (CCl ₄)	- 95 ± 11	- 27 ± 11	0.9809	4
MoCl ₅	SiO ₂	55 (CCl ₄)	- 60 ± 5	- 13 ± 7	0.9830	5
Mo	SiO ₂	55 (CCl ₄)	- 77 ± 5	- 26 ± 6	0.9978	3
Mo	SiO ₂	25 (CCl ₄)	- 65 ± 4	- 21 ± 5	0.9909	6
MoCl ₅	SiO ₂	25 (CCl ₄)	- 66 ± 11	- 12 ± 13	0.9444	6
MoCl ₅	SiO ₂	15 (CCl ₄)	- 56 ± 3	- 10 ± 3	0.9935	7
Mo	SiO ₂	15 (CCl ₄)	-115 ± 19	- 66 ± 22	0.9858	3
(MoOCl ₃)	SiO ₂	25 (CCl ₄)/ 15 (H ₂ O)	- 91 ± 5	- 26 ± 6	0.9914	7
(MoOCl ₄)	NaCl	90 (CCl ₄)	- 43 ± 3	17 ± 12	0.9865	5
MoCl ₅	NaCl	90 (CCl ₄)	- 72 ± 8	- 12 ± 7	0.9790	6
Mo	NaCl	90 (CCl ₄)	-136 ± 6	- 65 ± 6	0.9990	3
MoCl ₅	MgCl ₂	90 (CCl ₄)	- 68 ± 9	- 35 ± 12	0.9752	5
Mo	MgCl ₂	90 (CCl ₄)	-112 ± 8	- 62 ± 9	0.9916	5

TABLE I (continued)

Compound*	Surface	Partial pressure of reactive gas (mmHg)	ΔH_{ads} (kJ mole ⁻¹)	ΔS_{ads} (J mole ⁻¹ °K ⁻¹)	Regression coefficient	Number of points
MoCl ₅	CaCl ₂	90 (CCl ₄)	- 73 ± 3	- 21 ± 3	0.9942	13
MoCl ₅	CaCl ₂	90 (CCl ₄)	-100 ± 5	- 34 ± 5	0.9970	4
MoOCl ₄	YCl ₃	90 (CCl ₄)	- 48 ± 5	15 ± 6	0.9601	11
MoCl ₅	YCl ₃	90 (CCl ₄)	- 76 ± 3	- 28 ± 3	0.9925	16
MoOCl ₃	CsCl heated at 950 °K	90 (CCl ₄)	- 78 ± 6	- 30 ± 8	0.9928	5
MoCl ₅	CsCl heated at 870 °K	90 (CCl ₄)	- 76 ± 10	- 27 ± 12	0.9672	5
MoCl ₅	KCl, 1st series	90 (CCl ₄)	- 84 ± 4	- 40 ± 4	0.9955	3
Mo	KCl, 1st series	90 (CCl ₄)	-136 ± 25	- 81 ± 30	0.9376	6
(MoOCl ₄)	KCl, 2nd series	90 (CCl ₄)	- 41 ± 1	2 ± 1	0.9995	4
MoCl ₅	KCl, 2nd series	90 (CCl ₄)	- 83 ± 6	- 40 ± 3	0.9865	7
(MoOCl ₄)	KCl, HfCl ₄ coated	90 (CCl ₄)	- 42 ± 3	2 ± 4	0.9939	4
MoCl ₅	KCl, HfCl ₄ coated	90 (CCl ₄)	- 83 ± 7	- 38 ± 8	0.9815	5
Mo	KCl, HfCl ₄ coated	90 (CCl ₄)	-135 ± 42	- 78 ± 46	0.9085	3
MoCl ₅	KCl, K ₂ Cl ₃ treated	90 (CCl ₄)	- 78 ± 5	- 33 ± 7	0.9975	3
MoCl ₅	KCl (with KCl packed column)	90 (CCl ₄)	- 85 ± 8	- 41 ± 9	0.9886	5
Mo	KCl (with KCl packed column)	90 (CCl ₄)	-129 ± 39	- 71 ± 23	0.9773	4
(TcOCl ₃)	SiO ₂ , 1st series	90 (CCl ₄)	- 94 ± 9	- 29 ± 10	0.9678	8
TcCl ₄	SiO ₂ , 1st series	90 (CCl ₄)	- 94 ± 2	- 24 ± 2	0.9992	7
TcOCl ₄	SiO ₂ , 1st series	90 (CCl ₄)	- 50 ± 1	- 3 ± 1	0.9999	3
TcCl ₅ **	SiO ₂ , 1st series	90 (CCl ₄)	- 65 ± 5	- 13 ± 5	0.9924	7
TcCl ₄	SiO ₂ , 2nd series	90 (CCl ₄)	- 85 ± 5	- 15 ± 5	0.9961	4
TcOCl ₄	SiO ₂ , 2nd series	90 (CCl ₄)	- 52 ± 4	- 6 ± 4	0.9891	6
TcCl ₅	SiO ₂ , 2nd series	90 (CCl ₄)	- 67 ± 3	- 15 ± 4	0.9935	5
TcOCl ₄	SiO ₂ , carbon modified	90 (CCl ₄)	- 44 ± 2	2 ± 2	0.9925	11
TcCl ₅	SiO ₂ , carbon modified	90 (CCl ₄)	- 62 ± 3	- 10 ± 4	0.9956	5
TcOCl ₄	SiO ₂	Together 15, 25, 55, (CCl ₄)	- 52 ± 2	- 5 ± 2	0.9907	15
TcCl ₅	SiO ₂	Together 15, 25, 55 (CCl ₄)	- 69 ± 2	- 17 ± 2	0.9954	16
(TcOCl ₃)	SiO ₂	25 (CCl ₄) 15 (H ₂ O)	-101 ± 7	- 37 ± 7	0.9934	5
TcCl ₄	SiO ₂	25 (CCl ₄) 15 (H ₂ O)	- 87 ± 15	- 16 ± 17	0.9709	4
TcOCl ₄	NaCl	90 (CCl ₄)	- 50 ± 1	2 ± 2	0.9997	6
TcCl ₅	NaCl	90 (CCl ₄)	- 69 ± 1	- 9 ± 1	0.9997	5
TcCl ₄	MgCl ₂	90 (CCl ₄)	- 62 ± 6	- 26 ± 8	0.9821	7
TcCl ₅	MgCl ₂	90 (CCl ₄)	- 67 ± 12	- 12 ± 14	0.9222	5
TcCl ₅	CaCl ₂	90 (CCl ₄)	- 79 ± 1	- 28 ± 2	0.9985	11
TcCl ₄	C ₂ Cl ₂	90 (CCl ₄)	- 80 ± 6	- 21 ± 7	0.9845	6
TcOCl ₄	CaCl ₂	90 (CCl ₄)	- 70 ± 5	2 ± 5	0.9862	7

(Continued on p. 326)

TABLE I (continued)

Compound*	Surface	Partial pressure of reactive gas (mmHg)	ΔH_{ads} (kJ mole ⁻¹)	ΔS_{ads} (J mole ⁻¹ °K ⁻¹)	Regression coefficient	Number of points
TcCl ₄	YCl ₃	90 (CCl ₄)	- 66 ± 3	- 17 ± 3	0.9877	16
TcCl ₅	YCl ₃	90 (CCl ₄)	- 75 ± 6	- 17 ± 7	0.9785	8
TcOCl ₄	YCl ₃	90 (CCl ₄)	- 68 ± 3	- 1 ± 2	0.9953	8
TcCl ₅	KCl, 1st series	90 (CCl ₄)	- 80 ± 4	- 33 ± 6	0.9933	5
TcCl ₄	KCl, 1st series	90 (CCl ₄)	- 85 ± 10	- 20 ± 12	0.9789	6
TcCl ₅	KCl, 2nd series	90 (CCl ₄)	- 79 ± 14	- 36 ± 17	0.9285	7
(TcOCl ₄)	KCl, 2nd series	90 (CCl ₄)	-102 ± 20	- 43 ± 20	0.9819	3
TcCl ₅	KCl (with KCl packed column)	90 (CCl ₄)	- 74 ± 4	- 26 ± 5	0.9951	5
TcCl ₅	KCl, HfCl ₄ treated	90 (CCl ₄)	- 79 ± 12	- 36 ± 14	0.9301	3
TcCl ₄	KCl, HfCl ₄ treated	90 (CCl ₄)	- 81 ± 12	- 22 ± 13	0.9775	4
(TcOCl ₃)	CsCl heated at 950 °K	90 (CCl ₄)	-100 ± 5	- 44 ± 5	0.9977	4
TcCl ₄	CsCl heated at 950 °K	90 (CCl ₄)	- 75 ± 7	- 27 ± 8	0.9918	4
ZrCl ₄	SiO ₂ , 1st series	90 (CCl ₄)	- 97 ± 12	- 54 ± 8	0.9465	9
ZrCl ₄	SiO ₂ , carbon modified	90 (CCl ₄)	- 81 ± 4	- 18 ± 5	0.9955	5
ZrCl ₄	YCl ₃	90 (CCl ₄)	- 90 ± 6	- 32 ± 6	0.9892	7
TeCl ₄	SiO ₂ , 1st series	90 (CCl ₄)	- 54 ± 2	- 6 ± 2	0.9946	11
TeCl ₄	SiO ₂ , 2nd series	90 (CCl ₄)	- 57 ± 5	- 7 ± 6	0.9669	11
TeCl ₄	SiO ₂ , carbon modified	90 (CCl ₄)	- 43 ± 3	- 8 ± 3	0.9689	16
TeCl ₄	Graphite	90 (CCl ₄)	- 83 ± 8	- 17 ± 5	0.9462	13
TeCl ₄	Graphite, RuCl ₃ treated	90 (CCl ₄)	- 74 ± 14	- 15 ± 14	0.8347	15
TeCl ₄	SiO ₂	55 (CCl ₄)	- 57 ± 3	- 5 ± 3	0.9943	7
TeCl ₄	SiO ₂	25 (CCl ₄)	- 51 ± 3	5 ± 4	0.9803	11
TeCl ₄	SiO ₂	15 (CCl ₄)	- 41 ± 3	14 ± 4	0.9751	11
Te	SiO ₂	25 (CCl ₄)/ 15 (H ₂ O)	- 81 ± 13	- 27 ± 15	0.9209	9
TeCl ₄	NaCl	90 (CCl ₄)	- 70 ± 15	- 18 ± 17	0.9029	6
TeCl ₄	MgCl ₂	90 (CCl ₄)	- 70 ± 3	- 17 ± 3	0.9946	9
TeCl ₄	CaCl ₂	90 (CCl ₄)	- 75 ± 4	- 26 ± 5	0.9820	12
TeCl ₄	YCl ₃	90 (CCl ₄)	- 73 ± 3	- 18 ± 3	0.9917	18
TeCl ₄	CsCl heated at 950 °K	90 (CCl ₄)	- 42 ± 3	10 ± 3	0.9940	5
TeCl ₄	CsCl heated at 870 °K	90 (CCl ₄)	- 90 ± 4	- 54 ± 6	0.9960	5
TeCl ₄	KCl, 1st series	90 (CCl ₄)	- 85 ± 8	- 38 ± 10	0.9785	6
TeCl ₄	KCl, 2nd series	90 (CCl ₄)	- 79 ± 10	- 36 ± 12	0.9703	6
TeCl ₄	KCl, HfCl ₄ treated	90 (CCl ₄)	- 77 ± 2	- 32 ± 2	0.9985	5
TeCl ₄	KCl, RuCl ₃ treated	90 (CCl ₄)	- 72 ± 19	- 24 ± 22	0.9108	5

* The compounds listed are the most probably formed species: where we consider that the assignment might not be complete; if modified, the formula is enclosed in parentheses. If there is insufficient evidence of the identity of the compound, only the element is stated.

** Although TcCl₅ has not yet been positively identified, we think that the pentachloride is probably formed under the experimental conditions and the observed chromatographic properties indicate that this compound is a pentachloride; therefore, we are convinced that the observed compound is TcCl₅.

denum and technetium have higher coordination numbers in the condensed phases than in the gas phase;

(2) there is a correlation between the complexing abilities of the solid phase and the experimental adsorption enthalpies (e.g., potassium chloride forms stronger complexes with niobium pentachloride than does sodium chloride and the adsorption enthalpy for niobium pentachloride is -75 kJ mole^{-1} on sodium chloride and $-101 \text{ kJ mole}^{-1}$ on potassium chloride);

(3) there is a correlation between adsorption enthalpies and entropies (see Fig. 2); this is to be expected as stronger chemical bonding causes a higher loss of enthalpy and a higher loss of entropy.

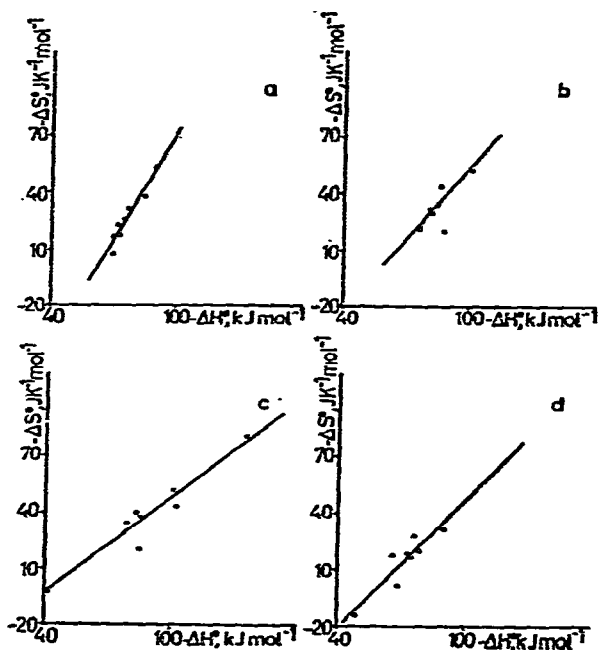


Fig. 2. Correlations between adsorption enthalpies and entropies. (a) TeCl_4 on different surfaces; (b) NbCl_5 on different surfaces; (c) different compounds on KCl ; (d) different compounds on YCl_3 .

Although a general trend for all adsorbent-adsorbate pairs can be recognized, the correlation between adsorption enthalpies and entropies is better for a given adsorbate on different adsorbents or, *vice versa*, for different adsorbates on a given adsorbent. This is demonstrated by the data in Fig. 2 and the values obtained by linear regression of these data (Table II). This may be explained by the effect of the individual geometry of the different surface complexes. As both the adsorbate and adsorbent have considerable influence on the geometry of the surface complex, better correlations can be expected when only one of them is varied than for a variation of both adsorbent and adsorbate. Consequently, the best correlations are obtained if adsorbents and adsorbates with similar properties and structures are

TABLE II

CORRELATIONS BETWEEN ADSORPTION ENTHALPIES AND ENTROPIES ($\Delta S_{ads} = a\Delta H_{ads} + b$)

Compound	a ($10^{-3} \text{ }^\circ\text{K}^{-1}$)	b ($\text{J } ^\circ\text{K}^{-1}\text{mole}^{-1}$)	Regression coefficient	Number of points
TeCl ₄ on different surfaces	1.86 ± 0.24	115 ± 19	0.9521	8
NbCl ₅ on different surfaces	1.28 ± 0.20	74 ± 17	0.9317	8
Different compounds on KCl	0.85 ± 0.11	38 ± 10	0.9532	8
Different compounds on YCl ₃	1.14 ± 0.21	67 ± 15	0.9126	8

compared (eg., the adsorption of a given compound on different ionic chlorides)*.

Further information can be obtained from a simplified statistical thermodynamic calculation. The adsorbed molecule has lost three degrees translational freedom and gained three degrees of vibrational freedom and an amount of configurational entropy due to the many possibilities of distribution of the adsorbed molecules on the surface. A comparison of calculated and experimental entropies indicates that the surface complex has gained one or more degrees of easily excitable vibrational freedom with frequencies in the range 10^{11} – 10^{12} sec⁻¹. This is a striking analogy to the well known gas-phase complexes, where the experimentally determined entropies of formation also indicate easily excitable vibrations. From this point of view, it is obvious that in addition to the strength of the bonding between chemisorbed molecules and the surface, the geometry and properties of both the surface and the chemisorbed molecule have a considerable influence on the various possible movements (vibration, rotations) of the chemisorbed molecules. Unfortunately, the experimental results do not allow a detailed interpretation of the surface complexes, as the errors in the experimental data obscure the fine detail required. Nevertheless, we think that it is reasonable to assume that the surface complexes have structures similar to those of their known complexes in bulk phases, e.g., niobium pentachloride has a six-fold chloride coordination in the surface complex with one of the chloride ligands supplied by the solid phase, and zirconium tetrachloride had a six-fold coordination with two of the chloride ligands supplied by the solid phase.

CONCLUSIONS

The inorganic gas chromatographic method described is promising for the investigation of gas-solid interactions at high temperatures with solid phases with very small surface areas and at extremely low surface coverages. It is possible to determine adsorption (chemisorption) enthalpies and entropies for the formation of inorganic surface complexes, which supplies information that gives a deeper insight into the mechanisms of the chemisorption of metal halides (or oxides, etc.).

The results suggest parallels between these "surface complexes" and the well known gas-phase complexes. It is to be hoped that further investigations of these

* Nevertheless, it should be mentioned that the general similarity of the enthalpy-entropy correlations points towards the uniformity of the chemisorption mechanism, that is, surface complex formation.

chemisorption phenomena will present results that are as interesting as the similar gas-phase complexes. An understanding of the chemisorption of volatile inorganic halides, oxides and similar compounds is the basis for many applications of the gas-solid chromatography of these compounds. We think that the method presented for the determination of adsorption data provides a useful means of collecting valuable information about the chemisorbed state, but additional methods can be applied in order to obtain further complementary information about the interesting field of "surface complexes" of halides and similar compounds.

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