The Study of the Alloys of Platinum and Tin by Chemisorption

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Studies of the adsorption of carbon monoxide, ethene, and deuterium on platinum, Pt_3Sn, PtSn, and $PtSn_2$ have identified significant differences between the surface and the bulk composition of the alloys, in agreement with current theories. After annealing *in vacuo*, the surfaces are considerably enriched in tin, this enrichment occurring mainly at the expense of the subsurface zone, which thus becomes correspondingly enriched in platinum. Carbon monoxide adsorption induces a reversible surface enrichment in platinum. Temperature-programmed desorption experiments reveal that as the proportion of tin in the alloys increases, desorption of the above-mentioned gases becomes progressively easier. This suggests a loosening of the chemisorptive bond caused by the adsorbing platinum atoms becoming surrounded by tin atoms (the "ligand effect"). Adsorption of ethene on platinum leads to extensive auto-hydrogenation of the ethene and to carbon formation; Pt_3Sn and PtSn, however, adsorb ethene reversibly.

INTRODUCTION

Within the framework of a general study of bimetallic systems in our laboratory, we have tried to characterize such systems by a method of selective chemisorption. Such a technique should provide information not only on the surface composition of the alloys, which is important because of the "ensemble effect" (*1*) in chemisorption and catalysis on alloys, but also on the extent to which alloying affects the thermodynamics of adsorption/desorption phenomena, which is of importance in view of the "ligand effect" (*1*). For the determination of the surface composition, selective chemisorption, which involves only the outermost atoms of the adsorbent, is superior to such techniques as ESCA and Auger spectroscopy where the relevant signals come from a zone near the surface comprising an unknown number of atomic layers. Theories of surface composition have been derived

for biphasic alloys (*2*) and for solid solutions and ordered alloys (*3–6*).

In our present work we have investigated ordered alloys of platinum and tin. This system is interesting for two reasons: (i) The theories of Van Santen (*4*) and Williams (*5*) predict that for these alloys the outermost layer sould be strongly enriched in tin, whereas the atomic layer below the surface should be enriched in platinum. Consequently Auger and ESCA data, which refer to both layers, should indicate a lower degree of tin enrichment than chemisorptive titration of the outermost layer. For the PtSn system, Auger and ESCA have been published by Bouwman *et al.* (*7, 8*).

(ii) The platinum–tin alloys are stoichiometric compounds, i.e., alloy formation is exothermic. If this exothermicity is due to filling of the *d*-orbital of platinum, it may be expected that chemisorption bonds

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with the Pt atoms are significantly affected by alloying Pt with Sn [the so-called "ligand effect" (1)]. This would become manifest in the temperature-programmed desorption (TPD) spectra; for a given gas and an identical heating program, the TPD peaks would then be shifted by alloying. However, since neither the direction nor the amount of peak shifting can be predicted with certainty in the present state of the theory, experimental data are required to verify the intuitive concept. This formed the second incentive for the present work.

The choice of the adsorbates was governed by the following requirements: (i) The adsorbate should be adsorbed by only one of the constituent metals; (ii) the metal atoms in the surface of the alloy should be covered to a precisely known extent so that the number of adsorbed species can be used to estimate the surface composition; (iii) the adsorption process should not drastically alter the composition of the surface.

We believed that low-temperature adsorption of hydrogen, carbon monoxide, and ethene satisfied these requirements to an acceptable extent. In the work with hydrogen, we actually used the deuterium isotope in order to prevent interference of the measurements with the hydrogen background in the quadrupole mass filter.

The evaluation of chemisorption titration data requires an assumption concerning the number of surface atoms "counted" by an adsorbed molecule. In the case of carbon monoxide adsorbed on platinum and platinum–tin alloys one can either assume that the $CO/Pt_{surface}$ ratio is the same for both pure platinum and the alloys; or that on the alloys $CO/Pt_{surface} = 1$ whereas it is <1 for pure platinum because of some multicentered ("bridged") adsorption. Support for the latter view was obtained with palladium–silver alloys by Soma-Noto and Sachtler (9) who found that with increasing dilution of palladium in silver, adsorption of carbon monoxide became increasingly

linear, i.e., $CO/Pd \rightarrow 1$. It is conceivable that the preference for the linear complex will be even larger for alloys of platinum and tin, since these, unlike palladium–silver, form ordered phases, i.e., the Pt atoms are preferentially surrounded by Sn atoms. For the numerical evaluation of our data we have, therefore, used $CO/Pt_{surface} = 1$. If future work provides quantitative data on the actual contribution of multicentered CO complexes on PtSn alloys, it will be easy to correct the present data accordingly.

A second complication is caused by impurities, which may influence the $CO/Pt_{surface}$ value; we have therefore included some measurements on platinum and platinum–tin films deposited under ultrahigh vacuum. The results were entirely consistent with the measurements on powders, and this may be used as an argument that impurities have played a minor role.

With regard to the thermodynamic data to be obtained from the TPD technique, it was anticipated that the high temperatures required might induce a surface reconstruction leading to chemisorption-induced aggregation of platinum atoms in the surface. This phenomenon, easily identified by subsequent chemisorptive titration, complicates the evaluation of the TPD spectra, although it does not invalidate the statement that of two alloys the one with the desorption peak at the higher temperature must also have the strongest chemisorptive bond with the gas in question, provided that the differences in peak position are large.

METHODS

Adsorption/Desorption Apparatus

A diagram of the adsorption/desorption apparatus is given in Fig. 1. The space enclosed between valves 3 and 4 and one side of the pressure transducer head is calibrated and has a volume of about 50 cm³. The reactor volume plus calibrated

volume is about 100 cm³. With the pressure transducer working under optimum conditions (i.e., with no background noise), we can measure a pressure difference of 3.50 Pa (corresponding to 0.2 cm on the MV recorder). The maximum pressure tolerance is 667 Pa for the particular diaphragm used. We can thus detect manometrically a minimum uptake of 350 ml/Pa (273 K) under ideal circumstances. The main source of error is the lack of uniformity of temperature, particularly in the head. This holds especially for adsorptions, during which the temperature of the reactor is quite different from that of the rest of the apparatus. This may introduce small errors in the expansion factors. For small uptakes, therefore, the amount adsorbed is not only determined manometrically but also measured by evacuating all the nonadsorbed gas through the mass spectrometer with simultaneous counting of the number of nonadsorbed gas molecules.

The system is designed in such a manner that the metal powder can be oxidized and reduced *in situ*, with oxygen and hydrogen, and kept in the high-vacuum part where the ionization pump maintains a vacuum better than 10^{-6} Pa. This is sufficient to protect the cleaned surface from contamination for a long time.

Our apparatus allowed the adsorbed species to be thermally desorbed and their quantity to be measured in a highly sensitive quadrupole mass spectrometer.

Adsorbates

As the adsorbates we employed deuterium, carbon monoxide and ethene. Other interesting compounds, such as NO, N_2O, H_2S, and SO_2, could not be used because, among other reasons, they give rise to dissociative adsorptions, lead to low, varying coverages, and lack specificity for one of the metals. The gases used were of the highest purity available and were employed without further purification. After each adsorption/desorption experiment the sam-

1-6   HIGH-VACUUM
        BAKEABLE VALVES
7-15 NON-BAKEABLE VALVES
A   OIL-DIFFUSION PUMP
B   TWO-STAGE ROTARY
        VACUUM PUMP
C   PIRANI GAUGE
D   PHILIPS PENNING
        GAUGE
E   MERCURY-DIFFUSION PUMP
F   FURNACE
G   ION PUMP
H   TABLE
MS   MASS FILTER
P   PRESSURE TRANSDUCER (PACE PD 70)
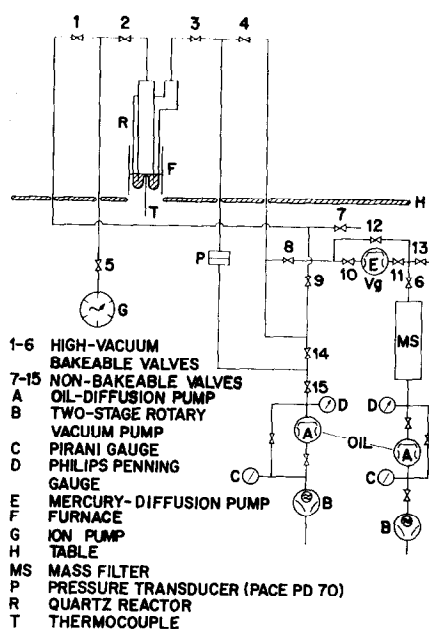R   QUARTZ REACTOR
T   THERMOCOUPLE

FIG. 1. Adsorption/desorption apparatus. Items above the table are baked.

ples were thoroughly cleaned by treating them with pure oxygen at 723 K and subsequently reducing them with hydrogen at 773 K to prevent progressive build-up of poisonous material.

Platinum–Tin Alloys

We used three unsupported, well-defined platinum–tin compounds, Pt₃Sn, PtSn, and PtSn₂, and, for reference purposes, finely dispersed platinum powder ("platinum black"). The compounds were prepared by melting the spectroscopically pure metals together under an argon atmosphere in a quartz ampoule. The product was then ground to a particle size of about 1 μm in a tungsten carbide ball-mill.

The absence of phases other than that corresponding to the overall composition was verified by X-ray diffraction. The specific surface areas of the powders were estimated with a Perkin–Elmer/Shell BET adsorption apparatus using nitrogen. They were very small, usually between 0.2 and 0.5 m²/g.

Upon comparing the pertinent literature data with our own results on the adsorption of deuterium (D_2) on platinum black after different cleaning procedures with oxygen and deuterium, we concluded that traces of carbon and sulfur were adequately removed from the surface by the following treatment.

The sample was heated in oxygen (1 bar) at 723 K, and subsequently in deuterium (1 bar) at 748 K, each time for 2 hr, after which it was evacuated at 10^{-6} Pa for 16 hr at 773 K to remove dissolved deuterium.

We expect that this procedure can also be used for cleaning Pt_3Sn and PtSn, because Auger and carbon burn-off experiments, in which the carbon dioxide formed was monitored by glc, showed that the carbon and sulfur contaminants were not as strongly adsorbed on these systems as on pure platinum.

Before each adsorption experiment the reactor containing metal powder was rapidly cooled to 300 K. In this way we hoped to freeze the equilibrium surface composition of the alloys at 773 K.

Procedure

In an adsorption/desorption experiment, a known amount of gas was admitted into the reactor containing 1–2 g of the metal powder and the adsorption was measured manometrically with the pressure transducer. The reactor was then cooled under the remaining gas in either a Dry Ice/alcohol or a liquid nitrogen bath and the adsorption was measured again. The equilibrium pressure during adsorption was always between 26.7 and 200 Pa. In this region the amount of gas adsorbed was independent of pressure. Subsequently, valve 3 (see Fig. 1) was closed and the calibrated volume was evacuated via valve 12 and through the mass spectrometer, with simultaneous counting of the gas molecules. The reactor was then evacuated in the same way, at low temperature. Comparison of these two volumes (with expansion factors as estimated with helium) indicates whether gas can be pumped off at this low temperature. The adsorption was allowed to continue for 20 min, before cooling for 20 min and evacuation to a background pressure of $<4 \times 10^{-4}$ Pa. The same was then heated in a programmed manner at a rate of ca. 5 K/min. TPD spectra were obtained by counting the number of desorbing gas molecules using the mass spectrometer. In this procedure valve 12 was closed and the high-speed mercury-diffusion pump was used to evacuate the reactor, preventing pressure build-up which would result in readsorption of the gas molecules.

Although heating can result in the genesis of different adsorbed species or in dissolution of the adsorbed gas in the lattice, we were able to identify those desorption processes that are kinetically distinguishable. Heating was stopped at 790 K to prevent excessive sintering of the surface.

The above procedure also allows us to calculate the mass balance of the adsorbate, defined as (total mass)$_{in}$ − (total measured mass)$_{out}$, which would have to be zero within experimental error.

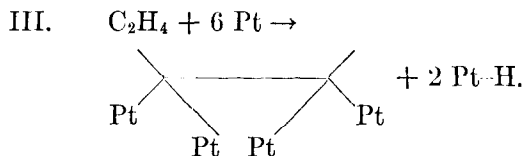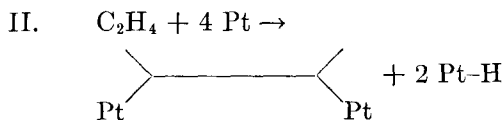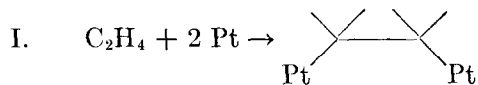RESULTS AND DISCUSSION

Adsorption and Surface Composition

1. Platinum/deuterium. At 77 K only a small, nonreproducible amount of deuterium was taken up; at 123 K adsorption became appreciable; and above 313 K deuterium was again taken up at a low rate (possibly due to dissolution). A total coverage of the platinum surface with deuterium ($D/Pt_{surface} = 1$) was achieved by adsorption at room temperature followed by cooling in liquid nitrogen. The results were well reproducible and the adsorption behavior of platinum observed by us agreed well with what has been described in the literature.

2. Platinum/carbon monoxide. With carbon monoxide it was impossible to achieve a total coverage of the platinum surface under our conditions, as could be predicted

from literature data. This low coverage is one of the arguments for the existence of several adsorption modes. On platinum, however, carbon monoxide seems to be adsorbed preferentially in linear form. On pure platinum films an ir absorption band at 1874 cm^{-1}, which is attributed to multicenter bonded species, can be detected only if the film is evaporated under a high pressure of carbon monoxide (10). Very recently Shai and Schlyarov (11) showed that, on very pure platinum foil in ultrahigh vacuum and at 200 K, a surface stoichiometry very close to $CO/Pt_{surface} = 1$ can be realized. At room temperature small carbon impurities on the surface decrease the maximum amount of carbon monoxide taken up. In one of our experiments we determined a $CO/Pt_{surface}$ ratio of 0.76 upon adsorption at room temperature and cooling to 77 K and after correction for the physically adsorbed species. (We considered as physically adsorbed those species that could be pumped off at 77 K.) Thus either there must still be impurities on our surface that do not effect the deuterium adsorption or, alternatively, powders do not react as a foil does.

At 77 K the total coverage, including the physically adsorbed species, was 0.93.

3. Platinum/ethene. Adsorption of ethene on platinum resulted in autohydrogenation of the ethene; using the mass spectrometer we identified hydrogen, methane, and ethane in the gas phase, partly during the adsorption and partly during the TPD. This confirms the findings of Komers et al. (12) and is consistent with the ir work of Morrow and Sheppard (13), who reported that ethene is adsorbed on platinum in the following ways:

I. $C_2H_4 + 2 Pt \rightarrow$ (ethylene bridging two Pt atoms)

II. $C_2H_4 + 4 Pt \rightarrow$ (ethylene bonded to two Pt) $+ 2 Pt\text{-H}$

III. $C_2H_4 + 6 Pt \rightarrow$ (ethylene bonded across Pt atoms) $+ 2 Pt\text{-H}.$

4. The alloys Pt$_3$Sn, PtSn, and PtSn$_2$. In interpreting the adsorptive behavior of the alloys Pt$_3$Sn, PtSn, and PtSn$_2$ we assumed that adsorption took place selectively; in other words, that deuterium, carbon monoxide, and ethene were adsorbed only on the surface platinum atoms. We based this assumption on literature data (14) which show that these gases are not adsorbed by tin. We have verified this by using an alumina loaded with 5% tin. Moreover, our results with Pt$_3$Sn and PtSn confirmed that tin atoms do not adsorb these molecules. For adsorptions at low temperatures where the migration of atoms in the solid phase is very slow, it is justifiable to assume that the adsorption process does not significantly alter the composition of the surface (as obtained after annealing for a long time at 773 K and subsequently quenching).

The adsorption experiments were carried out at room temperature, followed by cooling to 195 K (carbon monoxide and ethene) or 77 K (deuterium). The amounts of gas adsorbed and subsequently desorbed are given in Table 1. The desorption spectra for PtSn and Pt$_3$Sn are shown in Fig. 2 (carbon monoxide) and Fig. 3 (ethylene).

a. Carbon monoxide. If we simply assume that each adsorbed carbon monoxide molecule counts one surface platinum atom, then the surfaces of Pt$_3$Sn and PtSn must contain 44.1×10^{17} and 16.7×10^{17} atoms of Pt/m^2, respectively. These figures indicate a significant enrichment of the alloy surfaces in tin; if the surface and bulk compositions were the same and the density of atoms in the surfaces of the alloys were the same as that in the surface of pure platinum $(119 \times 10^{17}/m^2)$, the figures would be about 81×10^{17} and 49×10^{17}.

TABLE 1

Amounts of Gas Adsorbed on and Subsequently Desorbed from Platinum and Platinum–Tin Alloys

Alloy	Adsorbate	Number of molecules [($\times 10^{17}$)m^{-2}]		
		Adsorbed	Desorbed	Nondesorbable
Pt	CO	90.8	57.0	33.8
Pt$_3$Sn	CO	44.1	28.3	15.8
	C$_2$H$_4$[a]	15.7	15.7	—
	D$_2$	8.1	<8	Balance
PtSn	CO	16.7	11.8	4.9
	C$_2$H$_4$[a]	3.5	3.5	—
	D$_2$	1.9	<1.9	Balance
PtSn$_2$	CO	<1	<1	—
	C$_2$H$_4$[a]	—	—	—
	D$_2$	—	—	—

[a] In contrast with what was found in the case of pure platinum, no hydrogen, methane, or ethane was produced.

We are now able to compare the surface concentration of Pt in Pt$_3$Sn and PtSn as predicted by Van Santen's theory to those measured by Bouwman et al. using Auger electron spectroscopy and ESCA and by the present authors using chemisorption. The results are shown in Table 2. In calculating the data, two things are assumed: (i) the density of matter in the surface of the alloys is the same as in the
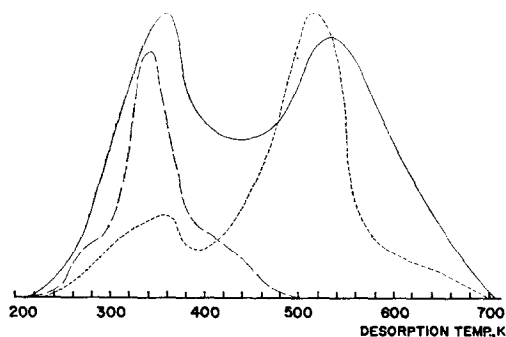

FIG. 2. Desorption of carbon monoxide from platinum (————), Pt$_3$Sn (– – –), and PtSn (— —).
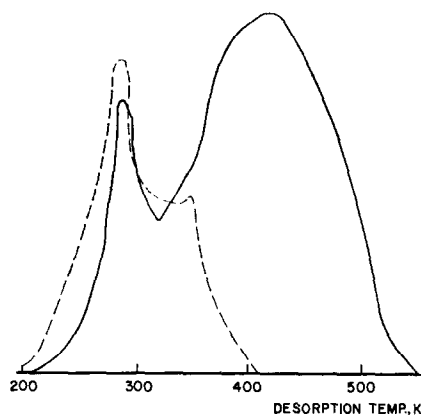

FIG. 3. Desorption of ethene from Pt$_3$Sn (————) and PtSn (– – –).

surface of pure platinum; (ii) the ratio, α, of the area occupied by a platinum atom to that occupied by a tin atom in the surface is 0.703; this figure is based on the atomic radii.

In order to obtain more realistic figures for the surface compositions of the alloys than can be calculated from Auger measurements alone, Bouwman et al. combined Auger spectroscopy with ESCA, in order to estimate the contribution of subsurface layers to the Auger data. The results, thus corrected, are shown in Table 2. From the table it can be seen that all the data support the theory and show an enrichment of the surface in tin. However, the values calculated from Auger/ESCA and chemisorption

TABLE 2

Measured Concentrations of Platinum Atoms in the Surfaces of Platinum–Tin Alloys

Alloy	Surface concentration of Pt [atoms ($\times 10^{17}$)m^{-2}]			
	Theory	Auger (uncorrected)	Auger/ ESCA[a]	Chemisorption
Pt$_3$Sn	49.1	68.3	55 (mean value)	44.1
PtSn	—	32.6	<24.3	16.7

[a] After correction for the subsurface concentration gradient.

measurements agree much more closely with the predicted figure than does that calculated from Auger measurements alone. The Auger results have a much larger standard deviation than those obtained by the chemisorption method.

The enrichment of the Pt$_3$Sn surface in tin occurs, according to Van Santen, by interchange of atoms in the surface with atoms in the layer just below the surface. In agreement with this conclusion, the uncorrected Auger data, which contain a contribution from the subsurface layers, indicate a considerably lower enrichment that the chemisorption data, which measure the outermost layers only The differences between these data are thus an experimental confirmation of theory. It is worthy of note that the Auger and ESCA data can only be made mutually consistent by postulating an inversion of the concentration gradient.

b. *Deuterium.* The most striking feature of the deuterium adsorption is the low coverage compared to that obtained with carbon monoxide. Dissociative adsorption of deuterium (or hydrogen) is likely to require two platinum atoms; moreover, it may be necessary for these to be adjacent. Van der Avoird (*15*) has shown that the nonactivated dissociative adsorption of a hydrogen molecule on two adjacent platinum atoms becomes an activated process when the distance between the metal atoms is enlarged; the potential well then becomes less favorable. Thus, it is possible that the introduction of a tin atom between the two platinum atoms makes dissociative adsorption an activated process.

However, adsorption experiments at higher temperatures (up to 375 K) did not in our experiments result in a greater coverage. At much higher temperatures it was clear that deuterium began to dissolve in the lattice. Dissolution also took place if we used deuterium atoms produced on a hot filament in our experiments with alloy films; this could perhaps be reduced by using deuterium atoms with low kinetic energy.

The covering of single platinum atoms by migrating deuterium atoms produced by dissociative adsorption on dual sites might also be an activated process. Molecular adsorption of hydrogen on platinum is very weak and is therefore absent except at extremely low temperatures; see, for example, the work of Lewis and Gomer (*16*). Therefore, a larger fraction of the platinum atoms in the surface might be covered by carbon monoxide than by deuterium. This extremely low adsorption of hydrogen by platinum–tin alloys is not shown by platinum–gold and nickel–copper alloys. The surface compsition of the latter alloys can be determined by titrating the active atoms with hydrogen, as was shown by Kuyers et al. (*17*) and Van der Plank and Sachtler respectively).

An alternative explanation of the adsorptive behavior of platinum–tin alloys towards hydrogen would be that there was a strong ligand effect, resulting in a drastic lowering of the heat of adsorption of hydrogen on the platinum atoms of the alloy surface. Indeed, both the heat of alloy formation and the difference in the electronegativities, i.e., the work functions, of the constituent metals are much larger for the Pt-Sn system than for NiCu or PtAu alloys. It is, therefore, quite conceivable that in the case of PtSn a much more pronounced electron transfer (from Sn to Pt) will occur than in the other alloy systems mentioned, and in consequence the heat of hydrogen adsorption might be alterned more severely for the PtSn alloys.

If the effects of tin on the dissociative adsorption of deuterium and on the migration of deuterium atoms are severe, the deuterium molecules adsorbed should count only multiple platinum sites, (i.e., dual sites, and, hence, their number should be equal to the number of ethene molecules adsorbed. However, the amount of deuterium adsorbed is much smaller, being approxi-

mately one-half of the amount of ethene adsorbed.

c. *Ethene.* In contrast with what was observed in the case of pure platinum, no hydrogen, methane, or ethane was produced upon adsorption of ethene on the platinum–tin alloys studied. This was also found by Komers *et al.* (*12*) after partial poisoning of a platinum surface with carbon monoxide. It is obvious therefore that extended aggregates of neighboring platinum atoms do not exist in the surfaces of these alloys; the majority of the platinum atoms are separated from each other by tin atoms.

Desorption and Energetic Effects

1. *Platinum/deuterium.* The desorption spectra showed four maxima (see Fig. 4): at 153, 263, 323, and above 623 K, in agreement with data reported by Tsuchiya *et al.* (*19, 20*). The reproducibility of the spectra was very sensitive to variations in the experimental conditions, in particular in the temperature program, and the time constant of the heat transfer from furnace to platinum. In each experiment, the total amount of deuterium desorbed was smaller than the amount adsorbed, the deficit (up to 28% of the amount adsorbed) depending on the history of the sample. Thus, prolonged evacuation of the sample prior to an adsorption/desorption experiment led to the largest deficit. After several successive

ADSORPTION TEMP.
———   −196 °C
————   −141 °C
—·—   − 60 °C

100   200   300   400   500   600   700
DESORPTION TEMP., K

Fig. 4. Desorption of deuterium from platinum.

adsorption/desorption experiments without prolonged evacuations, the deficit became very small and had only a slight influence on the amount of gas adsorbed in subsequent experiments. The amount of deuterium adsorbed, moreover, did not depend on whether the so-called δ-deuterium (corresponding to the high-temperature peak) had been desorbed from the sample, i.e., whether the desorption had been carried out at up to 523 K or to 773 K. All these facts, and a thorough analysis of Tsuchiya's paper, led us to the conviction that the high-temperature desorption peak arises from dissolved deuterium. Additional strong evidence for this can be found in a recent paper of Paál and Thomson (*21*). However, all previously published work shows that our conditions of adsorption should give surface coverages of one deuterium atom for every surface platinum atom, without dissolution. Hence, we have to conclude that the dissolution occurs during the desorption process. This was indeed confirmed in an experiment in which platinum powder, after adsorption of deuterium at low temperature, was heated in a closed system. A pressure drop was observed at about 315 K. Thus, dissolution at elevated temperature is a major complication in applying the TPD technique to desorption of hydrogen.

2. *Platinum/carbon monoxide.* Figure 3 shows a typical TPD spectrum. The spectrum of pure platinum is characterized by two desorption maxima appearing between 260 and 380 K and between 500 and 600 K. Not all the adsorbed species could be desorbed on heating up to 790 K, there being a deficit of 37.2%. [This was also found by Jakobith and Hugo (*22*).] An oxygen treatment, however, removed the remaining adsorbed carbon monoxide from the platinum surface. We assume that this carbon monoxide was not dissolved, since it strongly affected a subsequent adsorption. Jakobith and Hugo suggest that it is bridge-bonded carbon monoxide.
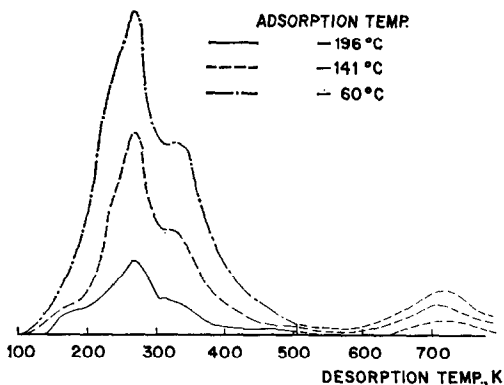
3. Platinum/ethene. Autohydrogenation of the ethene prevented a satisfactory application of the TPD technique in this case.

4. The alloys Pt₃Sn and PtSn. a. *Carbon monoxide.* If we compare the alloys Pt₃Sn and Pt₃Sn (Table 1), we can see that it was easier to desorb the carbon monoxide from the alloy containing the greater proportion of tin i.e., PtSn. The temperature at which most of the desorbable carbon monoxide is removed from the Pt₃Sn is only a little different from that for platinum, but it is nevertheless lower.

The interpretation of these desorption spectra is not straightforward. We assume that the two maxima at 360 and 540 K in our desorption spectrum for carbon monoxide on platinum correspond to the α_2 and β_1 maxima reported by Winterbottom (*23*), although the physical significance of these peaks is uncertain. Adams has demonstrated (*24*) the influence of adsorbate-adsorbate interactions on the TPD spectrum by computer simulation, and it is possible that the α_2 maximum might be caused by CO–CO interaction in the adsorbed layer. Bonzel and Ku (*25*) arrived at the same conclusion in their flash desorption studies of carbon monoxide on platinum partially covered with sulfur. If we assume this, the position of the β_1 maximum must reflect the activation energy for desorption, and thus, roughly, the heat of adsorption of carbon monoxide on platinum. It is clear from Fig. 3 that the heat of adsorption of carbon monoxide on Pt₃Sn is slightly different from that of carbon monoxide on platinum. However, the main effect of the dilution of the platinum atoms with tin atoms is not the shift in the position of the α_2 peak but the decrease in the intensity of the β_1 peak, indicating a decrease in the number of Pt ensembles responsible for this type of adsorption. In line with this assumption we ascribe the adsorption to pairs of adjacent platinum atoms, this interpretation also being consistent with adsorption data for deuterium and ethene.

The shift in peak position shows that the heat of adsorption of carbon monoxide is much lower on PtSn than on Pt₃Sn, indicating a strong "ligand effect." The low-temperature desorption maximum seen previously has completely disappeared; apparently all platinum atoms in the surface are isolated from each other. We considered it a mere coincidence that the maximum desorption of carbon monoxide from PtSn occurred in the same region as the low-temperature maximum desorption from platinum. If immediately after an adsorption/desorption experiment carbon monoxide is again adsorbed, then the alloy behaves completely differently: it behaves as if it were almost pure platinum containing perhaps a little Pt₃Sn or PtSn. This observation is entirely consistent with a chemisorption-induced surface enrichment in platinum at the high temperature required for desorption of the carbon monoxide. In the presence of a carbon monoxide atmosphere, a surface reconstruction is known to occur easily (*26*). This phenomenon is fully reversible: Upon evacuation overnight at room temperature we again obtain the TPD spectrum characteristic of the alloy, since, as we have shown, in equilibrium under vacuum the alloy surface must be enriched in tin. If we assume, as did Jakobith and Hugo, that the nondesorbable species are multiply adsorbed, then we must conclude that on platinum-tin alloys these species are formed only upon raising the temperature during the desorption process.

b. *Deuterium.* Because the level of deuterium adsorption is very small, and because deuterium dissolves in these alloys at higher temperatures (as it does in platinum) the TPD technique could not be applied fruitfully in this case.

c. *Ethene.* The TPD spectrum consists of two desorption maxima. The low-temperature desorption peak is more pronounced

in the case of PtSn than Pt₃Sn, indicating a lower integral heat of adsorption. Mass spectrometrically, only ethene could be detected in the desorbing gas.

Kinetics of Desorption

We have tried to analyze and interpret the TPD spectra in terms of numbers of different sites, each characterized by a desorption rate constant and an activation energy for desorption. The basic assumption that has to be made so that a model (simple enough to be handled by a computer) can be applied successfully, is that the desorption rate can be described by a rate constant of the Wigner–Polanyi type. Physically this means that no surface–adsorbate reactions, surface reconstructions or adsorbate–adsorbate interactions occur during the desorption process. Yet, even then the applicability of a thorough kinetic analysis is still rather doubtful. Without a careful study of the kinetic parameters of the system the results would have no physical meaning (*27–29*).

Unfortunately, the above requirements are not satisfied for our system. In the case of deuterium, dissolution of the adsorbed gas takes place during the desorption process; in addition, the information obtained arises only from a very small number of sites in the alloy surface.

With carbon monoxide, the desorption is accompanied by serveral complicated processes: (i) adsorbate–adsorbate interactions; (ii) surface reconstructions (the replacement of a tin atom from the surface by a platinum atom from a layer next to the surface under the influence of the strong CO-Pt interaction); (iii) possibly, a surface–adsorbate reaction (proposed by Jakobith and Hugo):

$$2\ Pt{=}C{=}O \rightarrow \begin{matrix} Pt \\ \diagdown \\ \diagup \\ Pt \end{matrix} C{=}O + CO\ \nearrow \ .$$
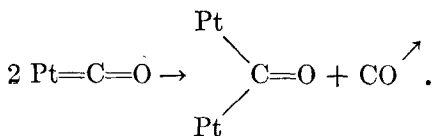
We have carried out an analysis of the PtSn/carbon monoxide desorption spectrum with the help of a computer, but we do not consider the results to be meaningful because the pre-exponential factors and activation energies in the rate constants for desorption found in this analysis were too small to be physically realistic. Even an experiment with pure platinum (a comparison with Winterbottom's work) did not give realistic results if we tried to analyze the spectrum in terms of only a few different sites, characterized by a few rate constants and activation energies.

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