ever, we feel that a qualitative interpretation of the influence of a chemisorbed film may be based on the following lines.

It is assumed that these isotherms represent the start of a multi-layer condensation process, that is, the 'S-shaped' isotherms of the Brunauer–Emmett–Teller theory. Again, following the Brunauer–Emmett–Teller treatment, we assume an average heat of adsorption on the clean surface to be E_1 for the first layer and E_L for subsequent layers, where E_L is approximately, if not exactly, equal to the heat of liquefaction of the adsorbate. Let the average heat of physical adsorption on the chemisorbed film be E'_1 for the first layer, and E_L for subsequent layers. In general, $E'_1 \neq E_1$, but providing $E'_1 > E_L$, then, though the isotherms for the clean and contaminated surfaces will not exactly correspond, nevertheless the point B and V_m values will be approximately the same. We suggest that this is the case in curve III for chemisorbed oxygen and the CO_3-complex. Indeed, the isotherms here indicate that $E'_1 > E_1$ at low coverages, a fact which lends itself to interesting speculation.

On the other hand, if $E'_1 < E_L$, then effectively no condensation will occur, at low relative pressures, on that fraction of the surface which is covered with the chemisorbed film ; and the isotherm and V_m value will correspond to the bare portion of the surface only. This, we suggest, occurs in curve II, where approximately 20 per cent of the surface is covered with chemisorbed carbon monoxide and the decrease in adsorption of krypton (and butane) is of that magnitude.

The question arises as to the likelihood of E'_1 being less than E_L in this case, that is, of the heat of adsorption of krypton on chemisorbed carbon monoxide being less than the heat of liquefaction of krypton. It is, of course, fairly easy to show that the van der Waals attraction between an isolated 'gas-phase' carbon monoxide molecule and a krypton molecule would be less than that between two krypton molecules. If we assume that on chemisorption the polarizability, 'characteristic energy' and dipole moment of the carbon monoxide molecule are not markedly increased, then it is quite probable that $E'_1 < E_L$. Conversely, if these isotherms are accepted as evidence that $E'_1 < E_L$, then it is possible to draw some qualitative inferences as to the nature of the chemisorbed state of carbon monoxide.

It is obvious that these very simple observations do not in any way depend on the more quantitative aspects of the Brunauer–Emmett–Teller theory which have recently been questioned[4]. Certain implications of the above treatment are being examined both theoretically and experimentally, and will be published in due course.

We are indebted to Prof. W. E. Garner for much helpful discussion on this subject.

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Association Reaction of Methyl Radicals

The nature of the bimolecular radical reaction which terminates the chains in the high-temperature photodecomposition of acetaldehyde will only be shown by analysis. Assuming the reaction :

$$CH_3 + CH_3 \rightarrow C_2H_6,$$

the amount of ethane to be expected can be calculated by the graphical integration

$$\frac{k_1 R_0}{2K^2 p_0 \{1-\exp(-\alpha p_0)\}^{1/2}} \int_{p_0}^{p_1} \frac{\{1-\exp(-\alpha p)\}^{1/2}}{p} \, dp \approx \frac{k_1}{\varphi}\left(1 - \sqrt{\frac{p_1}{p_0}}\right)$$

where p_0 mm. acetaldehyde have been irradiated, decomposing at initial rate R_0, to a final acetaldehyde pressure p_1 mm. The light absorbed is given by $I = 1-\exp(-\alpha p)$; K is the overall reaction constant, where $R = KpI^{1/2}$; φ is the overall quantum yield, and k_1 is the quantum yield of the primary process,

$$CH_3CHO \xrightarrow{h\nu} CH_3 + CHO.$$

The amounts of ethane thus obtained are such that only mass spectrometry will detect and estimate them in the presence of considerable quantities of methane and carbon monoxide.

Analyses have been carried out on the products of prolonged photolysis (up to 24 hr. for at least 90 per cent decomposition) of 200 mm. acetaldehyde at various temperatures and with $I_0 \approx 10^{-10}$ $Nh\nu$. cm.$^{-3}$sec.$^{-1}$, $\lambda = 2537$–3130 A. Table 1 shows the results obtained (after removal of residual aldehyde).

Table 1

Temp. ° C.	Mole (per cent)				
	CO	CH_4	HCHO	H_2	C_2H_6
123 obs.	49·6 50·4	43·5 42·4	0·2 0·2	2·9 3·1	3·9 3·9
calc.	50·0	41·8	4·1		4·1
212 obs.	49·8	44·7	0·2	3·3	2·1
calc.	50·0	49·0	0·5		0·5
422 obs.	49·9	48·7	<0·1	0·9	0·5
calc.	50·0	59·0	<0·01		<0·01

Probable errors in analysis for formaldehyde, hydrogen and ethane are ± 0·2 mole per cent. The presence of formaldehyde is thus not definitely established.

Some preliminary analyses for ethane showed the same trend (see Table 2).

Table 2

Temp. ° C.	125	140	308
Ethane (obs.)	2·7	2·7	1·1
,, (calc.)	3·3	1·4	0·07

Some peaks of very low intensity at mass numbers 31, 40–46, 58, 60 indicated traces of other oxygenated compounds. In particular, upper limits of 0·2 and 0·05 per cent respectively can be given for glyoxal and diacetyl.

The presence of ethane is consistent with the assumed termination reaction ; though the calculated figure is subject to some uncertainties, particularly in the value to be given to k_1, the quantum yield of the primary process. Here we use $k_1 = 0·5$. The formaldehyde and hydrogen probably arise from side reactions,

$$\mathrm{CHO + CHO \rightarrow HCHO + CO}$$
$$\searrow \mathrm{H_2 + 2CO},$$

the material balance requiring that $p_{\mathrm{C_2H_6}} = p_{\mathrm{HCHO}} + p_{\mathrm{H_2}}$.

If the ethane does arise from the reaction between methyls, this excludes the reaction

$$\mathrm{CH_3 + CHO \rightarrow CH_4 + CO}$$

as the chain termination. On the other hand, it does not exclude the alternative mechanism in which formyl radicals propagate the chain, when the reaction between methyl radicals would be the side reaction. Nevertheless, the weight of evidence is for methyl radicals as chain carriers. If that is the case, the above analysis suggests that the termination is, in fact,

$$\mathrm{CH_3 + CH_3 \rightarrow C_2H_6}.$$

This view is further substantiated by the agreement between the constants determined, by the sector method, for the termination reaction in the photolyses of acetaldehyde[1] and of mercury dimethyl[2]. The observed frequency factors, of the same order as the collision frequency, do not, however, agree with the steric factor 5×10^{-3} found by Marcus and Steacie[3] for the same reaction.

We have recently learned that Danby, Buchanan and Henderson[4] have carried out, independently, extensive mass spectrometric analyses on the products of the reaction in its initial stages and have reached the same conclusion about the chain-ending process.

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Use of 95 per cent Ethyl Alcohol as a Solvent for Ultra-Violet Spectroscopy

In connexion with a problem on the determination of the ultra-violet absorption spectra of organic molecules dissolved in 95 per cent ethyl alcohol[1], it was necessary to determine the suitability of the alcohol as a solvent in the region of 2000 A. There is a report[2] that carefully purified 95 per cent ethyl alcohol[3] is suitable for the region of 2000 A., although no experimental results were given. Observations in this region have been reported by MacLean, Jencks and Acree[4] for ordinary commercial 95 per cent ethanol, and they find that unpurified alcohol is completely opaque in this region.

It seemed to be of interest, then, to determine the transmission of purified 95 per cent ethanol down to 2000 A. The results are shown in Table 1. The percentage transmission of the alcohol was determined with the aid of a Beckman quartz spectrophotometer equipped with a Nestor hydrogen lamp. The transmission of the alcohol at the various wave-lengths was measured against distilled water, and it was assumed that the transmission of the water in this region was 100 per cent. Column *a* gives the results for the transmission of the untreated commercial alcohol; column *b* is for the alcohol after refluxing with dilute sulphuric acid and distillation[2], column *c* after treatment of the acid-treated alcohol with silver oxide and distillation. Repetition of the purification procedure with this alcohol did not materially change the values reported in column *c*.

Table 1

λ (A.)	(*a*) % Transmission	(*b*) % Transmission	(*c*) % Transmission
2300	62	68·2	83·8
2250	54	59·2	76·5
2200	46	50	67·5
2150	36	40	57·5
2100	28·2	33·8	45·5
2060	17	18·5	29·2
2040	10·8	10·9	18·9
2020	5	5	9
2000			6

Pirlot[5] has recently described another method for the purification of alcohols for ultra-violet spectroscopy, consisting in treatment with iodine, removal of the iodine with zinc and then passage of an alkaline solution of the alcohol over a column of activated charcoal. The results for ethyl alcohol in the region of 2000 A. were not reported; but from the data for the transmission of methyl alcohol in this region, it would seem that the values for ethyl alcohol treated in this fashion would be similar to those reported now.

Table 2

λ (A.)	(*a*) % Transmission	(*b*) % Transmission
2300	75·5	79·8
2250	68·0	70·8
2200	60	62·3
2150	50·8	54·0
2100	30·0	43·0
2050	9·0	18·2
2020		9·1
2000		3·5

An investigation of the transmission of commercial absolute alcohol was also made. The results are shown in Table 2. Column *a* shows the transmission for the untreated alcohol; column *b* shows the transmission after refluxing with dilute sulphuric acid, distillation and treatment of the distillate with silver oxide. The first and last 15 per cent of each distillate was discarded.

On the assumption that the solvent should transmit at least 50 per cent of the radiation[2] to be suitable at any particular wave-length, it would appear that even carefully purified 95 per cent ethanol is not a suitable solvent for work below 2100 A., and absolute alcohol is not suitable below 2120 A.

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