CHROM. 14,650

GAS CHROMATOGRAPHIC STUDY OF SOLUTION AND ADSORPTION OF HYDROCARBONS ON GLYCOLS

II*. ETHYLENE GLYCOL

E. L. ARANCIBIA and J. A. CATOGGIO*

División Química Analítica, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 esq. 115, 1900 La Plata (Argentina)

(First received April 2nd, 1981; revised manuscript received November 13th, 1981)

SUMMARY

Adsorption at the gas–liquid interface is demonstrated in hydrocarbon–ethylene glycol systems. Thermodynamic properties of solution and adsorption at the gas–liquid interface of these systems were determined.

The retention behaviour of olefins in ethylene glycol was studied. Values of retention parameters obtained from experimental data are compared with values in the literature; possible causes of discrepancies are discussed.

The contribution of so-called Kelvin retention to the overall retention process was calculated and its significance for different systems is discussed.

INTRODUCTION

Thermodynamic parameters of solution and adsorption at the gas–liquid interface have been determined by several workers employing a chromatographic method[1-4]. Even though the precision thus attained is not as good as that obtained when gas–liquid partition is the only mechanism responsible for the retention process, the results have proved the validity of the approach.

Martin[5] was able to demonstrate that the adsorption at the gas–liquid interface contributed to the retention volume when non-polar solutes were eluted from columns containing a polar liquid phase; taking this effect into account, he formulated the following equation:

$$V_N^0 = K_L V_L^0 + K_A A_L^0 \tag{1}$$

where V_N^0 is the net retention volume per gram of packing, K_L is the gas–liquid partition coefficient, K_A is the adsorption coefficient at the gas–liquid interface, V_L^0 is

---

* For Part I, see ref. 9.

the volume of the stationary liquid and A_L^0 is the exposed surface of same liquid, these last two parameters being per gram of packing.

Some other ratios have been proposed[1,6–8] that take into account the effect of additional mechanisms besides those already considered by Martin. The incidence of a given mechanism depends on the nature of the system studied and on the stationary phase to solid-support ratio used. Thus, for instance, it has been shown that adsorption on the solid support is meaningless when more than 5 % of a hydroxylated liquid is used as the stationary phase[1,2].

Results obtained for the thermodynamic parameters of solution and of adsorption at the gas–liquid interface of hydrocarbons when using diethylene glycol (DEG) and triethylene glycol (TEG) have been published recently[9]. These two systems, within the range of stationary phase to solid support ratios used, exhibit two main mechanisms which contribute to the retention volume, viz., gas–liquid partition and adsorption at the gas–liquid interface.

The possibility of comparing the solvent properties of ethylene glycol (EG) with those of DEG and TEG, as well as a predictable higher adsorption at the gas–liquid interface, determined the selection of EG as the liquid phase in this work. The thermodynamic properties of solution and of adsorption at the gas–liquid interface of hydrocarbons in EG, calculated on the basis of the experimental data, are given here. The influence of the Kelvin retention effect[10,11] on the adsorption coefficient at the gas–liquid interface is also shown.

EXPERIMENTAL

The equipment employed and the procedure followed have been described in detail in a previous paper[9]; the only difference was the temperature range for the experiments, which in this work was between 18 and 28°C.

Columns and reagents

Stainless-steel columns of 1/4 in. O.D. were used, 50 cm long for aromatic hydrocarbons and 150 cm long for aliphatic hydrocarbons. In order to avoid losses of stationary phase a pre-column of the same material and diameter and 50 cm in length was used, filled with the highest percentage of stationary phase that was employed.

Chromatographic-grade EG (Carlo Erba, Milan, Italy) was used as the stationary phase, and 60–80 mesh Chromosorb P, acid-washed, as the solid support. Packings were prepared as described previously[9]; their characteristics are given in Table I. Hydrocarbons were at least 99 % pure and are listed in Table II.

RESULTS

The retention process for some of the hydrocarbons studied is due to a mixed mechanism, as shown in Fig. 1. When gas–liquid partition is the only effect responsible for the retention process, the graph should consist of straight lines converging to the origin; deviations obey to adsorption at the gas–liquid interface and, as can be seen, this effect is greater for aliphatic than for aromatic hydrocarbons.

Values of the gas–liquid partition coefficients were obtained as described previously[9], using areas calculated according to the proposal of Martire et al.[12]; they are

TABLE I

COLUMN CHARACTERISTICS AT 25°C

| Parameter	Value				
Length	50 cm, for aromatic hydrocarbons				
Stationary phase percentage	23.53	19.85	14.46	9.779	4.719
W (g of packing)	4.6444	4.2552	3.8814	3.6755	3.5480
V_L^0 (cm^3/g)	0.2120	0.1788	0.1303	0.0881	0.0425
A_L^0 (m^2/g)	0.335	0.499	0.756	1.01	1.34
Length	150 cm, for aliphatic hydrocarbons				
Stationary phase percentage	26.19	18.95	14.46	7.373	5.166
W (g of packing)	14.6453	12.7452	12.1827	11.9295	11.4936
V_L^0 (cm^3/g)	0.2359	0.1707	0.1303	0.0664	0.0465
A_L^0 (m^2/g)	0.213	0.546	0.756	1.16	1.30
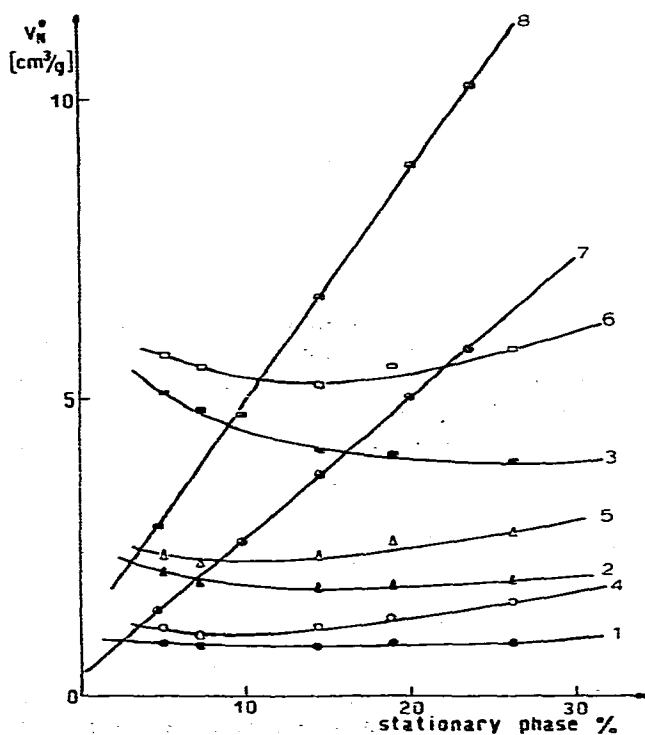
Fig. 1. Representative net retention volumes per gram of column packing as a function of stationary phase percentage: 1 = n-hexane; 2 = n-heptane; 3 = n-octane; 4 = 1-hexene; 5 = 1-heptene; 6 = 1-octene; 7 = benzene; 8 = toluene.

TABLE II

THERMODYNAMIC FUNCTIONS OF SOLUTION AT 25°C

Solute	$K_L \pm \sigma t$	γ^∞	ΔH_s^0 (kcal/mole)	ΔH_L^0 (Ref. 13) (kcal/mole)
n-Hexane	3.68 ± 0.10	598	5.9	7.5
n-Heptane	7.13 ± 0.22	1020	6.9	8.7
n-Octane	13.7 ± 0.5	1734	7.8	9.9
n-Nonane	27.1 ± 0.9	2853	9.1	11.1
1-Hexene	6.16 ± 0.15	290	6.1	7.4
1-Heptene	11.7 ± 0.3	507	7.2	8.6
1-Octene	21.4 ± 0.6	914	8.0	9.7
Cyclohexane	13.4 ± 0.2	253	6.2	7.9
Methylcyclohexane	16.0 ± 0.3	542	6.4	8.4
Ethylcyclohexane	33.1 ± 0.7	773	7.5	9.7
cis-2-Hexene	8.21 ± 0.19	268	6.1	7.5
Cyclohexene	29.2 ± 0.4	128	6.6	7.9
Isooctane	5.91 ± 0.21	1148	6.7	8.4
Isooctene	12.0 ± 0.4	674	6.8	8.8
Benzene	108 ± 2	32.3	6.8	8.1
Toluene	189 ± 3	61.7	7.6	9.1
Ethylbenzene	309 ± 6	112	8.1	10.1
n-Propylbenzene	482 ± 8	203	8.6	11.0
Isopropylbenzene	393 ± 7	184	8.4	10.8
o-Xylene	470 ± 7	107	8.3	10.4
m-Xylene	322 ± 5	124	8.0	10.2
p-Xylene	311 ± 6	123	8.1	10.1

listed in Table II, together with their respective 95% confidence intervals. Values obtained for the activity coefficients at infinite dilution and the standard partial molar enthalpies of solution (ΔH_s^0) are also given in Table II. Values of ΔH_s^0 were derived from the slope of the graph of $\ln K_L$ versus $1/T$, after subtracting the correction term $RT(1 - \eta T)$, (where η is the thermal expansion coefficient of the solvent); they correspond to the transfer of 1 mole of solute from an ideal vapour phase, at a pressure of 1 atm, to a hypothetical solution of unit molar fraction but obeying Henry's law. The value of the correction term in EG is 481 cal/mole at 25°C.

The standard molar free energy of adsorption at the gas–liquid interface was obtained from the equation

$$-\Delta G_A^0 = RT\ln(p^0/\pi^0) K_A \tag{2}$$

where p^0 is the pressure corresponding to the gaseous state and π^0 is the surface pressure of the adsorbed standard state. The standard states considered here are those defined by Kemball and Rideal[14]. Values of K_A at 25°C with their 95% confidence intervals for all of the hydrocarbons studied are given in Table III, together with the thermodynamic functions of adsorption at the gas–liquid interface.

TABLE III

THERMODYNAMIC FUNCTIONS OF ADSORPTION AT 25°C

Solute	$(K_A \pm \sigma_t \cdot 10^5 (cm)$	$-\Delta G_A^0$ (kcal/mole)	$-\Delta H_A^0$ (kcal/mole)	$-\Delta S_A^0$ (e.u.)
n-Hexane	5.36 ± 0.39	4.02	6.7	8.9
n-Heptane	13.4 ± 0.9	4.57	7.6	10.2
n-Octane	34.4 ± 1.1	5.12	8.6	11.8
n-Nonane	84.6 ± 2.3	5.66	9.7	13.6
1-Hexene	5.58 ± 0.48	4.05	6.6	8.5
1-Heptene	14.0 ± 1.2	4.59	7.5	9.9
1-Octene	36.1 ± 1.3	5.15	8.6	11.6
Cyclohexane	4.75 ± 0.83	3.95	5.9	6.5
Methylcyclohexane	10.9 ± 0.7	4.45	6.8	8.0
Ethylcyclohexane	27.1 ± 1.4	4.98	7.8	9.4
cis-2-Hexene	5.96 ± 0.61	4.09	6.6	8.5
Cyclohexene	5.89 ± 0.82	4.08	5.9	6.0
Isooctane	16.1 ± 0.9	4.67	7.5	9.4
Isooctene	19.8 ± 0.8	4.80	7.6	9.3
Benzene	8.94 ± 1.20	4.33	8.8	15.3
Toluene	25.9 ± 3.1	4.96	9.9	16.7
Ethylbenzene	65.4 ± 7.9	5.50	10.6	17.2
n-Propylbenzene	160 ± 20	6.03	11.5	18.2
Isopropylbenzene	130 ± 16	5.91	11.2	17.6
o-Xylene	82.0 ± 12.5	5.64	10.9	17.8
m-Xylene	72.0 ± 9.5	5.56	10.7	17.2
p-Xylene	70.7 ± 9.0	5.55	10.6	16.8

TABLE IV

PARTITION COEFFICIENTS AT 40°C

Solute	$K_{L(1)}$	$K_{L(2)}$	$K_{L(3)}$	$K_{L(4)}$
1-Hexene	3.92	4.18	3.5	2.58
1-Heptene	6.77	7.40	7.3	4.45
1-Octene	11.7	13.2	13.1	7.47
n-Hexane	2.38	2.63	—	1.47
n-Heptane	4.24	4.84	—	2.56
n-Octane	7.58	9.05	—	4.40
cis-2-Hexene	5.22	5.48	—	—
Cyclohexene	17.8	18.2	14.7	—
Benzene	65.1	65.7	47.8	—

DISCUSSION

The evaluation of the adsorption effect at the gas–liquid interface for the hydrocarbon–EG systems confirms and clarifies the suspicions of some authors about the existence of this effect[15].

In order to compare our results with those in the literature, we have extrapolated to 40°C the K_L values obtained from eqn. 1 and those calculated using the simple equation $V_N = K_L V_L$ for the maximum percentage of stationary phase tested.

Table IV lists the following: $K_{L(1)}$ are values of K_L free of surface effects, $K_{L(2)}$ are values of K_L for the maximum percentage of stationary phase, without correction because of adsorption, $K_{L(3)}$ are values taken from Muhs and Weiss[16] and $K_{L(4)}$ are values calculated from net retention volumes per gram of EG, at 40°C, as given by Ligny et al.[15].

Comparing values given by Muhs and Weiss[16], who used 22% of stationary phase, it is easy to conclude that it is necessary to consider the effect of adsorption at the gas–liquid interface; nevertheless, the results obtained for cyclohexane and benzene cannot be explained by this effect.

The values of K_L obtained from the data of Ligny et al.[15] are completely different from our $K_{L(1)}$ values. They used 40% of stationary phase under experimental conditions similar to those used in this work, except for the support (Kieselguhr) and they prepared the packing using methanol as the solvent, which was discarded in our study owing to significant losses of EG at 40°C.

Considering that the support could not affect their results, the values given by Ligny et al.[15] for V_N of hydrocarbons on EG cannot be supported by a rational basis.

Values of the activity coefficients at infinite dilution for the systems n-hexane–EG and benzene–EG, given in Table II, were compared with those in the literature at 25°C. Deviations as low as 4.5 and 4.0% were obtained between our values and those of Deal and Derr[17] derived from phase equilibrium data. The same systems showed deviations of 14.5 and 16.4%, respectively, between these reference values and those taken from chromatographic determinations without considering interfacial effects[18].

As in DEG and TEG, activity coefficients at infinite dilution of hydrocarbons in EG show great positive deviations from Raoult's law, the larger ones corresponding to aliphatic hydrocarbons and the smaller ones to aromatic hydrocarbons; the deviations increase with increasing number of carbon atoms within each particular family of hydrocarbons.

Larger deviations in EG than in DEG and TEG could be expected because of the greater association power of the first solvent, through the establishment of hydrogen bonds, thus making more difficult the dissolution of a hydrocarbon in such a medium.

On the other hand, the density of hydroxyl groups, which is higher in EG than in DEG and TEG, makes EG more effective in polarizing delocalized electrons in hydrocarbon molecules, and thus it facilitates the solubility of aromatic hydrocarbons because of their higher polarizability. This is in accordance with the values given in Table II, where it can be seen that the absolute solubility of aromatic hydrocarbons in EG is lower than that in DEG and TEG, as could be predicted from the already mentioned higher association in EG.

The great deviation obtained in the activity coefficients at infinite dilution calcu-

lated using the theory of regular solutions as modified by the equation of Weimer and Prausnitz[19] can be similarly adscribed to the high association of EG molecules.

Values of excess partial molar enthalpies (ΔH^e) calculated according to ref. 20 and excess partial molar entropies are given in Table II. According to these results, it could be concluded that the main energetic effect is due to the rupture of hydrogen bonds among glycol molecules.

Castells[3] obtained analogous results using formamide as stationary phase; he explained the high entropies of solution through a structural rearrangement of the solvent molecules around the solute molecules, similar to the behaviour of hydrocarbons in water reported by Frank and Evans[21].

According to Tyuzyo[22], the association in EG is comparable to that in formamide and, in spite of structural differences between these two solvents, there is some parallelism between the experimental results. It has not been possible to calculate the change in structural entropy with the equation proposed by DeVoe[23] for these two solvents because of the lack of available data to estimate the diameter of rigid spheres.

Selectivity values at 25 and 50°C for n-hexane–benzene and n-octane–benzene pairs, and capacity values of EG towards benzene, are given in Table V, together with the corresponding parameters in DEG and TEG[9]. The larger selectivities of EG compared with those of DEG and TEG for the two pairs considered, at both 25 and at 50°C, demonstrates its advantage as a solvent when trying to separate aromatic hydrocarbons; nevertheless, its poor capacity for dissolving these hydrocarbons discourages its application on an industrial scale.

Table III gives the values of the adsorption coefficients at the gas–liquid interphase at 25°C for all of the hydrocarbons studied, with their respective 95% confidence intervals. It can be seen that the precision of K_A values is directly related to the magnitude of the interfacial effect in the retention process.

Several workers[10,11,24] have claimed that it is necessary to consider the Kelvin effect in chromatographic beds, as a consequence of the curved surface of the stationary liquid in the pores of the solid support. Devillez et al.[10] took into account the Kelvin effect in the retention process for systems that show mixed mechanisms and concluded that in those instances, the so-called Kelvin retention affects the value of the adsorption coefficient at the gas–liquid interface.

TABLE V

SELECTIVITY AND CAPACITY TOWARDS BENZENE

Solvent	Temperature (°C)	Selectivity*		Capacity: $x_B = 1/\gamma_B^\infty$
		$\beta_{H/B}$	$\beta_{O/B}$	
Ethylene glycol	25	18.5	53.9	0.031
	50	17.6	48.3	0.037
Diethylene glycol[9]	25	17.0	38.6	0.155
	50	13.8	30.4	0.155
Triethylene glycol[9]	25	17.6	37.7	0.263
	50	13.4	27.8	0.263

* H = n-Hexane; O = n-octane; B = benzene.

TABLE VI

CONTRIBUTION OF KELVIN RETENTION (KR)

Solute	Stationary phase percentage	$K_L/K_L^\circ \cdot 10^2$	$KR/K_A\bar{A}_L \cdot 10^2$
n-Hexane	5.166	100.2	0.57
	26.19	100.5	3.56
n-Nonane	5.166	103.0	0.36
	26.19	100.7	2.24
1-Hexene	5.166	102.1	0.88
	26.19	100.4	5.46
Cyclohexene	5.166	101.7	3.17
	26.19	100.4	19.74
Benzene	4.719	101.9	5.71
	23.53	100.9	33.5
Ethylbenzene	4.719	102.1	3.0
	23.53	100.6	17.7

The Kelvin retention for some hydrocarbons representative of the families studied was determined and compared with the contribution of adsorption at the gas–liquid interface; values are given in Table VI, where ratios between the calculated partition coefficient and that for a plane surface[10,11] are also listed.

The results show, as Devillez et al.[10] had already stated, that the curved surface has a minimum effect on the partition coefficient and, consequently, activity coefficients at infinite dilution are practically unaffected because of this phenomenon. In contrast, adsorption coefficients at the gas–liquid interface for solutes of high solubility in the liquid stationary phase are definitely affected by the Kelvin retention; this applies to both aromatic hydrocarbons and cyclohexene, as shown in Table VI, where the Kelvin retention is important when it is compared with the adsorption at the gas–liquid interface. Nevertheless, because of the solubility of these hydrocarbons, adsorption at the gas–liquid interface exerts a very small effect, so that the precision of the resulting values is too poor to consider the correction due to Kelvin retention to be at all reliable.

Values for the Kelvin retention were calculated through the variation of $\bar{A}_L$ with $\bar{V}_L$ ($\bar{A}_L$ being the area of stationary liquid and $\bar{V}_L$ its volume, both per gram of solid support).

There are two reasons which made us to choose this means of calculating the Kelvin retention. On the one hand, there are discrepancies between the values of Conder and Young[11] and those of Devillez et al.[10] for the Kelvin retention although in both instances the values were obtained using the data for pore radius for Chromosorb P given by Saha and Giddings[25] and, on the other hand, there is agreement between equivalent series of values which both Conder and Young and Devillez et al. obtained through the procedure finally adopted here, taking values of $\bar{A}_L$ and $\bar{V}_L$ from Martin[5] when the behaviour of benzene in thiodipropionitrile was studied.

As already stated, the precision of K_A increases when the solubility of the solute in the stationary liquid phase decreases; the same considerations may be applied to the thermodynamic properties of adsorption given in Table VI.

The precision of the heats of sorption[1] and solution and of the heat of adsorp-

tion at the gas–liquid interface was calculated by applying Castells' reasoning[26] for some hydrocarbons representative of the families studied. Thus, the precision of the heat of sorption is ± 220 cal/mole in n-nonane, cyclohexane and benzene, and the precisions of the heats of solution are ± 300, ± 110 and ± 90 cal/mole for the same solutes, respectively. The precision of the heats of adsorption, however, is ± 1.200 cal/mole for benzene, ± 1.000 cal/mole for cyclohexane and ± 270 cal/mole for n-nonane.

The standard molar enthalpies of adsorption at the gas–liquid interface given in Table VI are smaller than the heat of liquefaction, except for the aromatic hydrocarbons, for which they are slightly higher; this allows us to conclude that hydrocarbons are retained at the glycol surface by very weak forces.

It can be seen that most of the adsorption entropy values at the gas–liquid interface listed in Table VI are more negative than the theoretical values calculated by Kemball and Rideal[14] for the entropic change associated with the transition of a three-dimensional gas to a two-dimensional gas; from this point it is possible to consider the adsorbed hydrocarbon molecules as a two-dimensional gas and include them in the mobile adsorption defined by Kemball[27].

ACKNOWLEDGEMENTS

REFERENCES

1 B. L. Karger, P. A. Sewell, R. C. Castells and A. Hartkopf, *J. Colloid Interface Sci.*, 35 (1971) 328.
2 B. L. Karger, R. C. Castells, P. A. Sewell and A. Hartkopf, *J. Phys. Chem.*, 75 (1971) 3870.
3 R. C. Castells, *An. Asoc. Quim. Argent.*, 64 (1976) 155.
4 R. K. Kuchhal and and K. L. Mallik, *Anal. Chem.*, 51 (1979) 393.
5 R. L. Martin, *Anal. Chem.*, 33 (1961) 347.
6 V. G. Berezkin, V. P. Pakhomov, V. S. Tatarinskii and A. M. Fateva, *Dokl. Akad. Nauk SSSR*, 180 (1968) 1135.
7 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
8 P. Urone, Y. Takahashi and H. G. Kennedy, *J. Phys. Chem.*, 73 (1970) 2326.
9 E. L. Arancibia and J. A. Catoggio, *J. Chromatogr.*, 197 (1980) 135.
10 C. Devillez, C. Eon and G. Guiochon, *J. Colloid Interface Sci.*, 49 (1974) 232.
11 J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, Wiley-Interscience, New York, 1979, Ch. 11, p. 509.
12 D. E. Martire, R. L. Pecsok and J. H. Purnell, *Trans. Faraday Soc.*, 61 (1965) 2496.
13 J. A. Riddick and W. B. Bunger, *Organic Solvents. Vol. II, Techniques of Chemistry*, Wiley-Interscience, New York, 3rd ed., 1970.
14 C. Kemball and E. K. Rideal, *Proc. Roy. Soc., London, Ser. A*. 187 (1946) 53.
15 C. L. De Ligny, T. van 't Verlaat and F. Karthaus, *J. Chromatogr.*, 76 (1976) 115.
16 M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, 84 (1962) 4697.
17 C. H. Deal and E. L. Derr, *Ind. Eng. Chem., Process Des. Develop.*, 3 (1964) 395.
18 P. Vernier, C. Raimboult and H. Renon, *J. Chim. Phys.*, 66 (1969) 429.
19 R. F. Weimer and J. M. Prausnitz, *Hydrocarbon Process.*, 44 (1965) 237.
20 E. F. Meyer, *J. Chem. Educ.*, 50 (1973) 191.
21 H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 13 (1945) 507.
22 K. Tyuzyo, *Bull. Chem. Soc. Jap.*, 30 (1957) 782.
23 H. DeVoe, *J. Amer. Chem. Soc.*, 98 (1976) 1724.

24 B. L. Karger and H. S. Liao, *Chromatographia*, 7 (1974) 288.
25 N. S. Saha and J. C. Giddings, *Anal. Chem.*, 37 (1965) 822.
26 R. C. Castells, *J. Chromatogr.*, 111 (1975) 1.
27 C. Kemball, in W. C. Frankenburg, V. I. Komarewsky and E. K. Rideal (Editors), *Advances in Catalysis*, Vol. II, Academic Press, New York, 1950, p. 233.