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## GAS CHROMATOGRAPHIC INVESTIGATION OF SOLUTIONS OF HYDROCARBONS IN PERHALOGENATED LIQUID POLYMER HYDROCARBONS AND OF ASSOCIATION PHENOMENA BETWEEN HYDROCARBONS AND ALUMINIUM CHLORIDE IN SOLUTION

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### SUMMARY

The association of some C<sub>5</sub>-C<sub>8</sub> alkanes, alkenes, and aromatic compounds with aluminium chloride, dissolved in liquid polytetrafluoroethene and polytrifluorochloroethene as inert and stable phases, has been investigated by means of a gas chromatographic elution method in the temperature range 50-80°C. For all the saturated and unsaturated compounds it was possible to measure association phenomena, depending on the amount of dissolved aluminium chloride and hydrocarbons, respectively, and their molecular structure.

The decrease in the vapour pressure of hydrocarbons present as solutes in a liquid phase containing a complexing substance leads to an increase in retention and is measurable in a headspace device.

The association constants calculated from the results of both methods are comparable.

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### INTRODUCTION

In the past decade there has been wide interest in complexing gas chromatography (GC) for theoretical purposes and analytical applications. A number of publications concerning the method and results have been reviewed<sup>1-3</sup>. The present paper aims at the investigation of the association properties of typical homogeneous Friedel-Crafts and polymerization catalysts, such as aluminium chloride. In previous papers<sup>4</sup> we reported the suitability of the method for investigating association phenomena and catalytic properties of Wilkinson-type catalysts [tristriphenylphosphinechlororhodium(I)], dissolved in 1,1- or 1,2-diphenylethane as stationary phases for hydrogenation reactions.

The measurement of association and complexing phenomena by GC methods requires stable non-complexing stationary phases. For the investigation of the association of dissolved aluminium chloride, polymer perhalogenated hydrocarbons are suitable, *e.g.* polytetrafluoroethene (PTFE) and polytrifluorochloroethene (PTFCE).

In this paper, the distribution properties of selected hydrocarbons as model

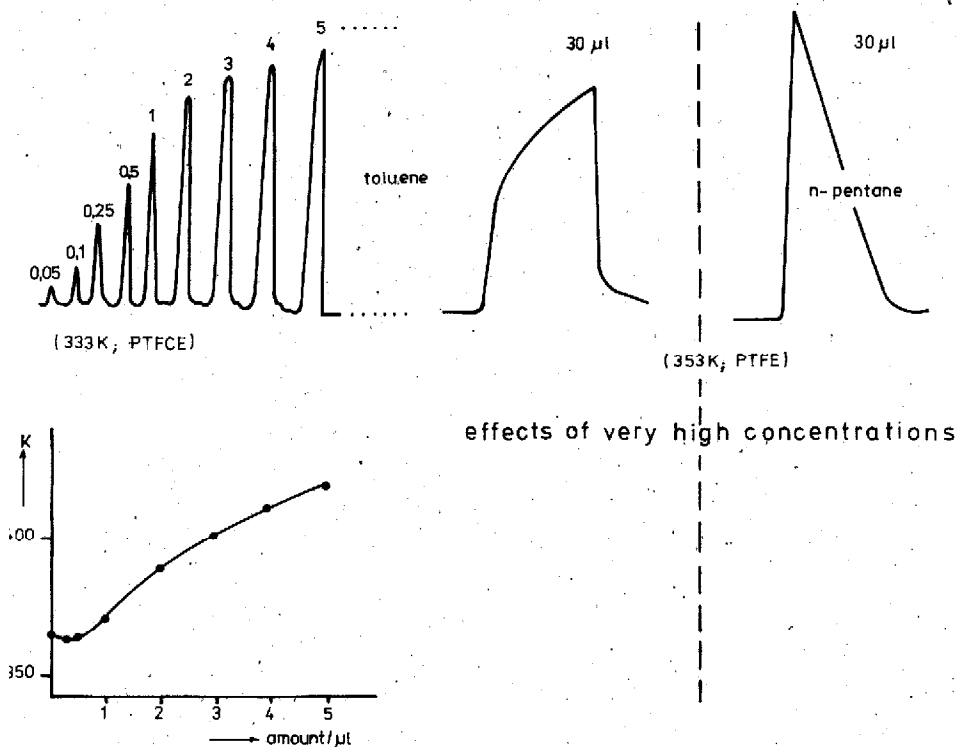


Fig. 1. Effect of amount of sample on peak shape and partition coefficient.

compounds are measured by means of GC in PTFE and PTFCE containing different amounts of aluminium chloride, as well as in pure PTFE and PTFCE. Thermodynamic quantities, especially enthalpies of the distribution of the model compounds between gas and liquid phase, follow from experimental partition constants at different temperatures. From another point of view, the experimental results can be discussed in terms of activity coefficients. In all cases of hydrocarbon partition and partition-association with aluminium chloride, the results can be strongly affected (Fig. 1, Table I) if experimental conditions, such as the amount of sample, the temperature, and the velocity of the carrier gas are not carefully chosen.

TABLE I  
RANGES OF ISOTHERM LINEARITY

Group of substances	Representative example	Range of isotherm linearity (limits) ( $\mu$ l)
n-Alkanes	n-Pentane	0.01-0.2
n-Alkenes	Hept-1-ene	0.01-0.1
Cyclic alkanes and alkenes	Cyclohexane, cyclohexene	0.01-0.5
Aromatics	Benzene	0.02-0.05

## EXPERIMENTAL

*Apparatus*

A Chromatron Model 18.3 gas chromatograph (Academy of Sciences of the G.D.R., Chromatron Production Department, Berlin, G.D.R.), equipped with a flame-ionization detector, was used. The retention times were corrected for dead-time in the GC system; a Hewlett-Packard Model 3380 A (Hewlett-Packard, Avondale, PA, U.S.A.) plotting integrator was used.

*Materials*









Hydrocarbons used as samples were commercial products from Fluka (Buchs, Switzerland). The liquid stationary phases were mainly telomers of PTFE (from Ferak, Berlin; average molecular weight:  $M \approx 730$  daltons, determined by means of a vapour pressure osmometer from Knauer, Berlin), or telomers of PTFCE, average  $M \approx 530$  daltons, synthesized at the Department of Chemistry, University of Greifswald. Both phases are suitable for dissolving aluminium chloride and for determining the chromatographic retentions of the  $C_5$ - $C_8$  hydrocarbons. The stationary phases are stable up to  $100^\circ\text{C}$  (Varian gas chromatograph-mass spectrometer, Model MAT 111; Varian Mat GmbH, Bremen, F.R.G.). PTFE is more stable than PTFCE.

The solid support was Chromosorb W-AW-DMCS (from Alltech Ass., IL, U.S.A., or Merck, Darmstadt, F.R.G.), covered with 3-20 weight-% liquid phase.

Aluminium chloride (99.99%, water-free, carefully sublimed before use, then stored in a glove-box) is a commercial product of UCB Producers, Brussels, Belgium (No. r.c.b. 85.078). The GC columns, containing dissolved catalysts or complexing substances in the liquid phase under inert conditions (nitrogen, argon), were prepared as described previously<sup>4</sup>.

TABLE II

ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR SOME HYDROCARBONS IN PTFE AND PTFCE

Solute	Solvent					
	PTFE			PTFCE		
	333.15 K	343.15 K	353.15 K	333.15 K	343.15 K	353.15 K
	1.14	1.1	1.01			
	1.23	1.21	1.12			
	1.30	1.32	1.31			
	1.20	1.13	1.12	1.15	1.11	1.08
	1.00	0.97	0.97	0.99	0.96	0.94
	0.95	0.96	0.88	0.90	0.86	0.80
	0.84	0.99	0.99	0.94	0.88	0.82
	1.11	1.03	0.97	1.04	0.94	0.92

## RESULTS AND DISCUSSION

Fig. 1 shows that the partition coefficient  $K$  for the distribution of the hydrocarbon solutes between the halogenated stationary phases (without added aluminium chloride) and the gas phase changes considerably when the injected amount of solute increases beyond, say,  $1 \mu\text{l}$ . As a result, the solute peak in the chromatogram becomes asymmetric. The partition coefficient may either increase or decrease with the injected amount of solute. In the former case, a concave distribution isotherm and fronting peaks are obtained. The second case leads to a convex distribution isotherm and

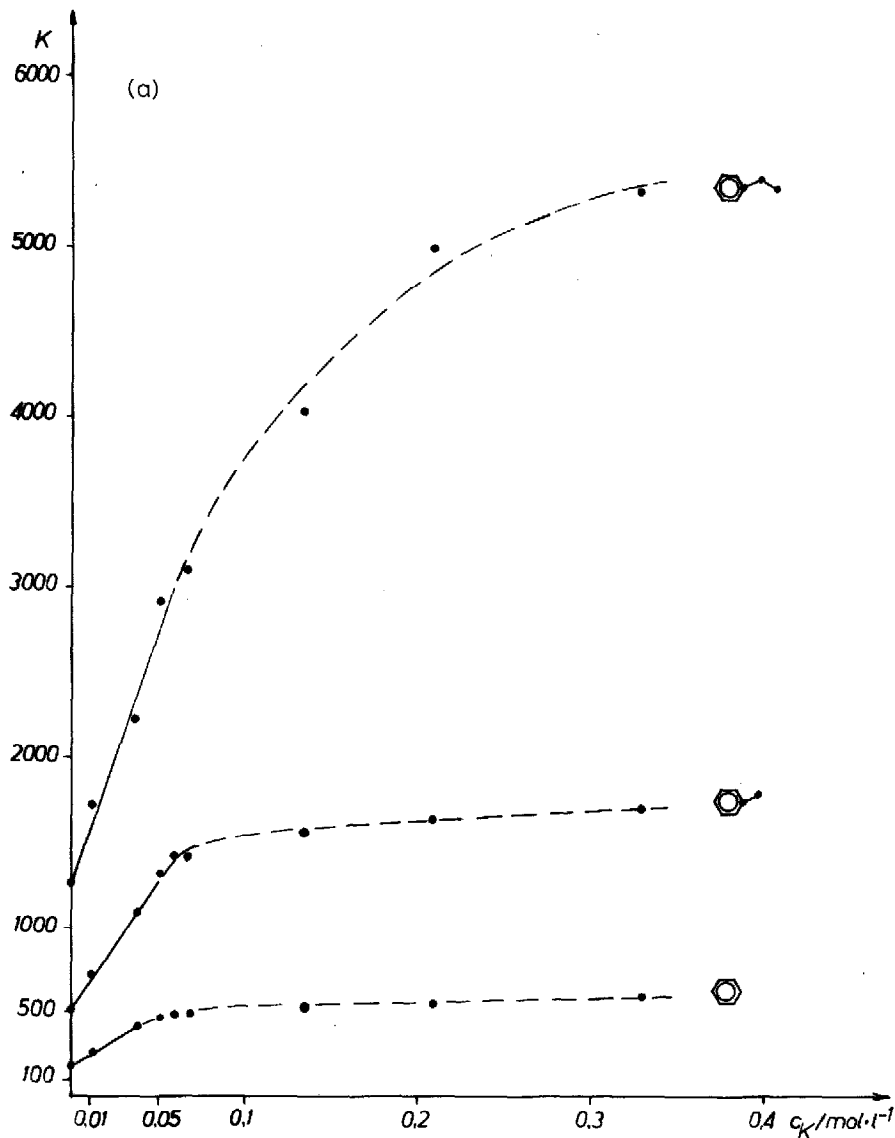


Fig. 2.

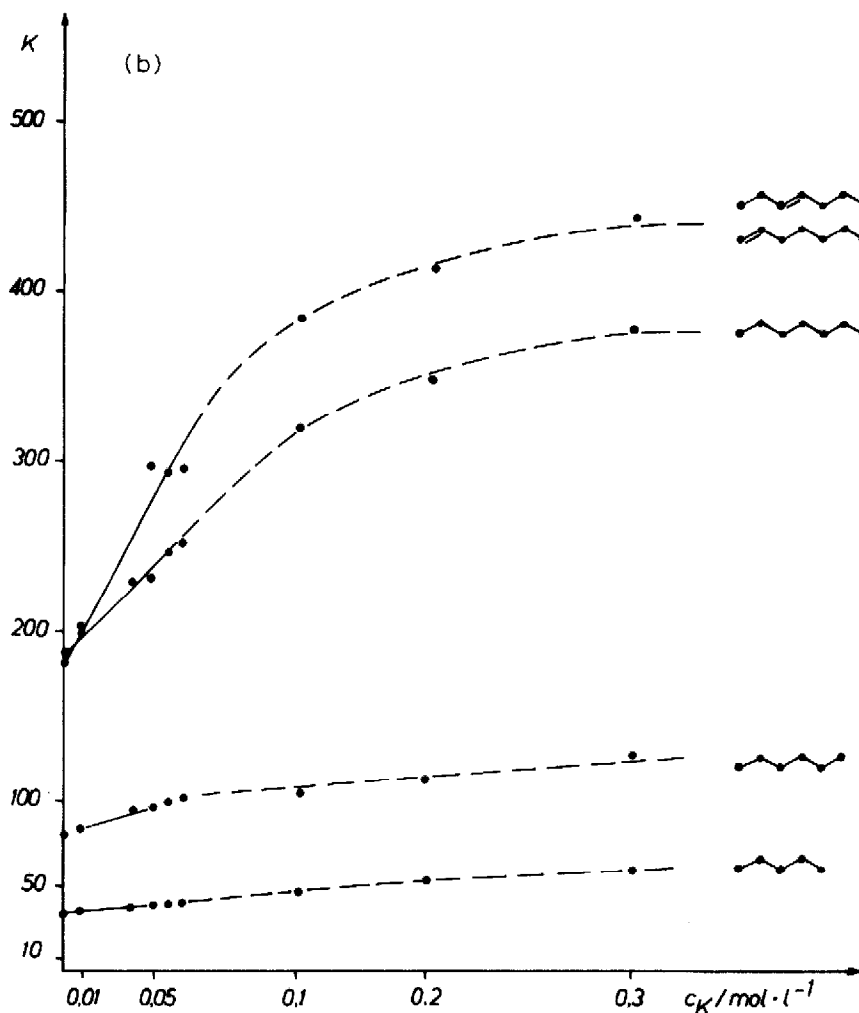


Fig. 2. Relation between partition coefficient and aluminium chloride concentration (temperature, 323 K). Effect of molecular size and structure: (a) high values of  $K$ ; (b) low values of  $K$ .

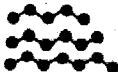



tailing peaks. Additionally, for very high amounts of solutes the sorption effect (variation of gas velocity with concentration) and the thermal effect (transient changes in temperature due to heat-of-sorption effects)<sup>1,2</sup> can strongly influence the shape of the peaks. For very small amounts of solute (say, 0.01  $\mu\text{l}$ ) a slight increase in  $K$  is observed, especially with aromatic solutes. This is probably due to adsorption either on the solid support or on the surface of the stationary phase.

Nevertheless, for a range of injected amounts of solutes  $K$  is about constant and the distribution isotherms are linear (Table I). From the retention times, measured in the linear range of the isotherms, activity coefficients at infinite dilution  $\gamma^\infty$  for some hydrocarbons in the PTFE and PTFCE stationary phases were calculated at eight temperatures (323–353 K). The values at three temperatures are given in Table II.

TABLE III

CONSTANTS  $K$  AND ENTHALPIES  $\Delta H$  (kJ mol<sup>-1</sup>) OF PARTITION AND FOR ASSOCIATION [ $K_K$ ,  $\Delta H_K$  (kJ mol<sup>-1</sup>)] OF HYDROCARBONS IN PTFE WITH DISSOLVED ALUMINIUM CHLORIDE (AT CONCENTRATION  $c_K$ )

Assumptions: Al<sub>2</sub>Cl<sub>6</sub> molecules in solution; 1:1 associates.

Solute	$K_0$ (333.2 K) $c_K = 0 \dots 0.038 \dots$	$K_K$ (333.2 K)	$\Delta H$ (323.2–353.2 K) $c_K = 0$	$\Delta H$ (323.2–353.2 K) $c_K = 0 \dots 0.038 \dots$
	28...30...	2.36	-16.9	-19.3
	71...78...	2.74	-19.4	-23.4
	164...206...	2.77	-22.6	-24.9
	78...94...	3.96	-20.5	-32.1
	181...221...	4.97	-23.6	-36.4
	471...607...	6.15	-30.4	-28.9
	108...120...	2.85	-28.8	-21.9
	134...155...	5.18	-28.1	-39.7
	126...160...	5.93	-24.7	-35.5
	136...264...	21.75	-28.6	-9.8
	430...829...	22.54	-32.4	-15.7
	820...1660...	23.05	-33.9	-9.8

When aluminium chloride is added to the stationary phase, enhanced  $K$  values are found (Fig. 2, Table III). The straight first part of the graphs of  $K$  vs. the concentration  $c_K$  of aluminium chloride is used to calculate 1:1 complex (or associate) formation coefficients<sup>5-12</sup> of the hydrocarbons with aluminium chloride. This was done in this paper according to Gil-Av and Herling<sup>5</sup>, with  $K = K_0(1 + K_K c_K)$ . The values are given in Table III. It appears that  $K_K$  increases with increasing molecular weight, and with increasing number of double bonds. It is especially large for aromatics. The influence of these two variables (molecular weight and number of double bonds) can be described approximately by a single variable<sup>13</sup>, *i.e.* the polarizability  $z = (\epsilon - 1)/(\epsilon + 2)$ . This is shown in Fig. 4.

The influence of the temperature on graphs of  $K$  vs.  $c_K$  is shown in Fig. 3. The slopes  $K_0 K_K$  of the straight line portions of the graphs are much smaller at 353 K than at 323 K. Apparently, complex formation is much less at the higher temperature, which points to a strongly negative enthalpy of complex formation. From data in the temperature range 323–353 K, the enthalpy of solution in the PTFE stationary phase  $\Delta H$  and the enthalpy of associate formation  $\Delta H_K$  were calculated. The values are given in Table III. The enthalpy of solution depends strongly on the molecular weight of the solute, but not on the number of double bonds. In contrast,  $\Delta H_K$  does not depend on the molecular weight. It is 9–18 kJ mol<sup>-1</sup> lower when one or two double bonds are present, but it is much higher for aromatics. From the high values of both  $K_K$  and  $\Delta H_K$  of the aromatics it follows that the entropy of complex formation is considerably less negative (*i.e.* more favourable) than for the other classes of compounds.

For some compounds, the results were verified by means of quantitative headspace analysis<sup>14,15</sup>. The device (see Fig. 5) is connected on-line with a gas chro-

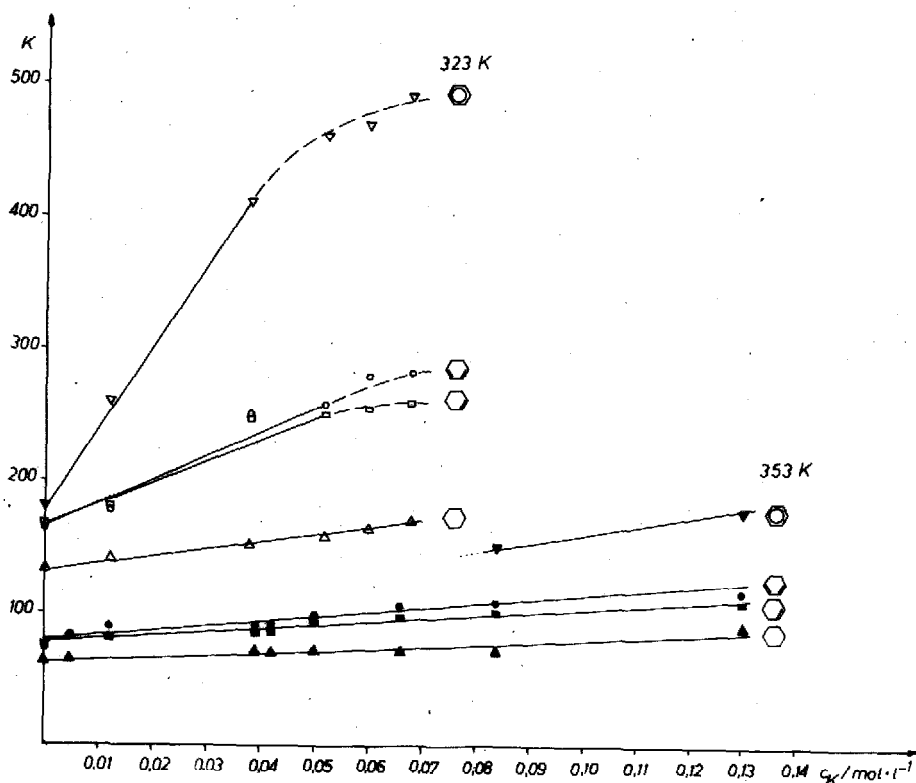


Fig. 3. Temperature dependence of the partition coefficient of some cyclic hydrocarbons in PTFE, containing aluminium chloride.

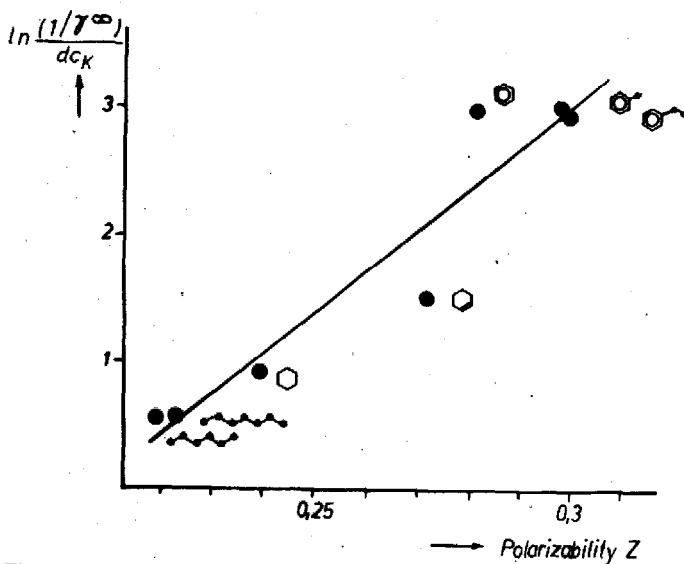


Fig. 4. Correlation between activity coefficient term at infinite dilution,  $\gamma^\infty$ , and polarizability,  $z$ , for some hydrocarbons.

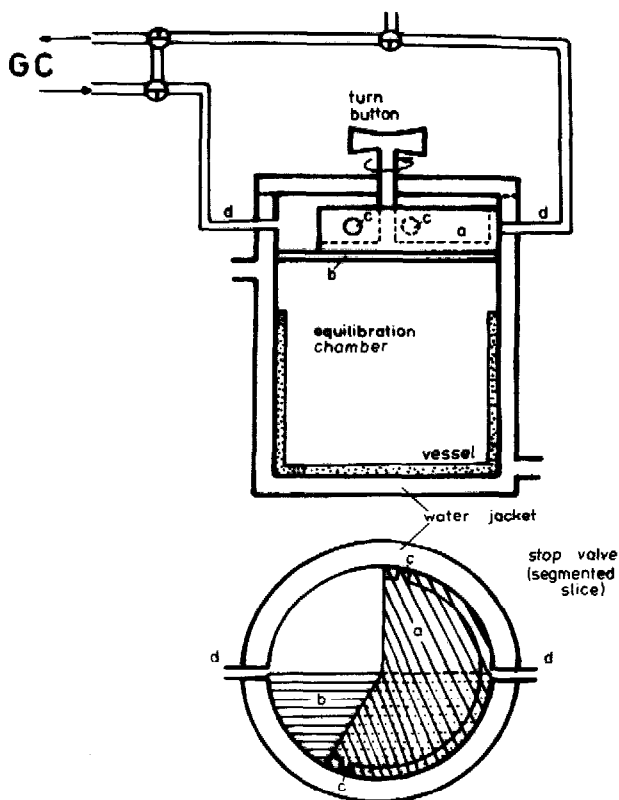


Fig. 5. Headspace device: chamber for equilibrating the liquid phase and the gas phase; teflon vessel for the liquid phase; stop valve with segmented movable (a) and fixed (b) slides for dividing the gas phase volume; holes (c) in the stop valve and pipes (d) for the carrier gas stream; thermostatted walls (water jacket).

matograph. The agreement was good, e.g. for cyclohexene:  $\Delta H_{K(GC)} = -39.7 \text{ kJ mol}^{-1}$ ;  $\Delta H_{K(headspace)} = -36.1 \text{ kJ mol}^{-1}$ .

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