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the thickness of the effusion foil and other parameters; (2) the cell constants determined by calibration with hexamethylbenzene, whose vapor pressures are known, coincided to ~5-10% with those determined with mercury.

Conclusions

The vapor pressure of dimethyl tetrachloroterephthalate has been measured and reported. It has been experimentally shown that (a) the Clausius-Clapeyron equation is followed, at least in the range 70-160 °C, (b) for each temperature and each hole diameter, a minimum effusion time is required, and (c) for each temperature the L/D ratio should be above a certain minimum. The effusion method seems to be more precise than the gas saturation method using the 916-TEA.

Acknowledgment

Linda Vargyas, Barbara Blackford, and Julia Black are thanked for the analysis of several samples for this work. Herbert Olson is thanked for the final preparation of the figures.

Glossary

p	saturated vapor pressure, torr
kcal	kilocalorie
T	absolute temperature, Kelvin
log	decimal logarithm
L	mean free path of the molecules of vapor inside the effusion cell, mm
D	effusion hole diameter, mm

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Chemical Equilibria in Condensed-Ring Systems. Isomerization Equilibria of *cis*- and *trans*-Decalin

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Equilibrium constants for the isomerization of *cis*- and *trans*-decalin were measured in the liquid phase at 6.4 MPa H_2 pressure and temperatures between 545 and 621 K. The enthalpy of isomerization was found to be −2.75 ± 0.05 kcal/mol and the entropy of isomerization was found to be −0.60 ± 0.07 eu. While these values agree with previously published data, absolute values of equilibrium constants differ by approximately 10%.

Catalytic hydroconversion is an important process for the upgrading of heavy crudes, residua, and coal liquids to distillate fuels. The multiphase reactions which occur during the hydroconversion of these highly aromatic feeds are both varied and complex; however, a key reaction is the addition of hydrogen to condensed polynuclear aromatic hydrocarbons. Furthermore, at the temperatures and pressures used in some processes, there exists a very real possibility of equilibrium limitations. Unfortunately, there have been very few chemical equilibrium measurements made on polynuclear aromatic hydrocarbons, so that it is difficult to predict a priori a possible limitation.

A survey of the literature shows that most of the experimental work to date has been done in the vapor phase for compounds containing one or two aromatic rings (*1-4*). One experimental liquid-phase study was also presented (*5*). A limited amount of work has been published on three-ring systems (*4*, *5*) but to date there are no data available on four-ring compounds. Similarly, there are no data available on alkyl-substituted polynuclear aromatics and little available on heterocyclic species. Since there are significant amounts of these present in coal liquids and residua, these data are also needed.

This paper describes a new experimental equilibrium cell which has been designed to obtain liquid-phase hydrogenation equilibrium data and presents experimental results for the isomerization equilibria of *cis*- and *trans*-decalin which differ from previously published experiments.

Experimental Section

The liquid-phase experiments described in this paper were carried out in the equilibrium cell shown in Figure 1. The entire experimental layout is shown in Figure 2. The cell was constructed of 316 stainless steel with an internal volume of approximately 60 cm^3. The bolted closure design utilized a self-energizing metal O-ring (UPA Components U6420-0275-SEB) to obtain the seal. The inside surface of the cell was coated with a Solaramic coating (Solar Turbines International, S-5210-2C) approximately 0.05 mm thick. Stirring was accomplished magnetically by using a combination hot plate/stirrer (Corning PC-351) with a glass-coated magnetic stirring bar (A. H. Thomas). The cell was wrapped with electrical heating elements and insulation on the top and sides; the temperature was controlled to ±0.5 °C of setpoint with a Doric Control:80 digital controller. Pressure was maintained constant with two Mity-Mite back pressure regulators to ±0.1 MPa of setpoint and the pressure was read digitally. The equilibrium cell was designed for temperatures up to 450 °C at 10 MPa. Direct sampling of the liquid phase was accomplished through a $^1/_8$-in. (3.18-mm) o.d. capillary dip tube (i.d. = 0.012 in.). Outside the cell this tube was connected to a microcapillary valve (Precision Sampling 460050) and a 7-cm needle from a 1-μL syringe. The total volume of the sampling system was calculated to be less than 10 μL. However, to prevent contamination of samples, 25-50 μL of liquid was withdrawn from the cell and discarded prior to taking each sample. A small volume sample was then withdrawn directly into a capped septum bottle containing 1 mL of *n*-heptane plus internal standard (*n*-decane). Samples were analyzed by gas chromatography on an HP 5834A GC equipped with FID using a 10-ft. (3-m) column packed with 3% Dexil 300

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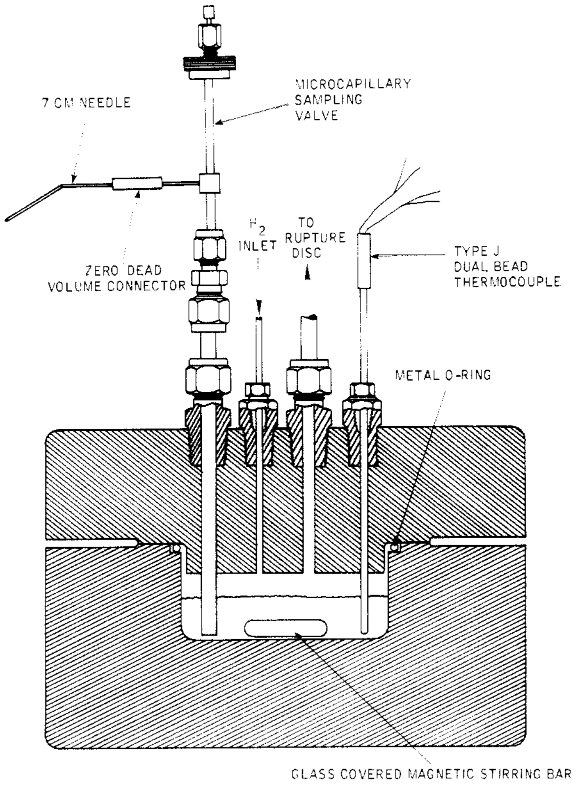

Figure 1. High-temperature equilibrium cell.

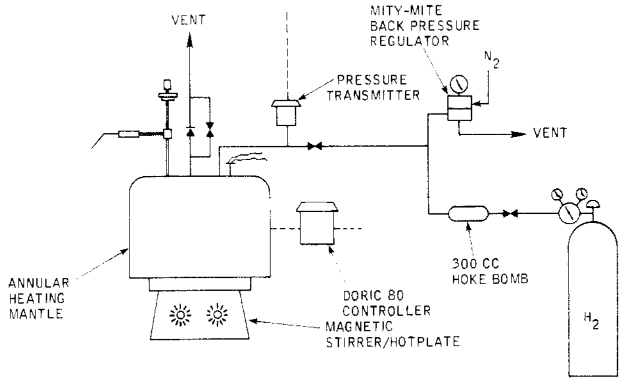

Figure 2. Overall schematic of equilibrium cell system.

on 100/120 Supelcoport. Helium was used as the carrier gas at 40 cm^3/min. The oven temperature was held constant at 100 °C for 3 min and programmed at 2 °C/min to 120 °C. Calibration factors for *cis*- and *trans*-decalin were determined by using a mixture of known composition and found to be equivalent (i.e., the relative response factor of *cis*- and *trans*-decalin was 1.01). *trans*-Decalin (K & K Laboratories) was analyzed and found to be 99.4% pure and was used without further purification. The catalyst used in this study was 5% palladium on carbon (MCB PX0010) and was reduced prior to use in hydrogen at 300 °C.

In a typical experiment the equilibrium cell was loaded with 0.4 g of catalyst and 20–25 cm^3 of *trans*-decalin or a mixture of *cis*- and *trans*-decalin. The cell was bolted closed and pressure tested with hydrogen to 1.5 times the operating pressure. The system was flushed several times with hydrogen and brought up to the desired pressure. It was then heated to the desired temperature and maintained at that temperature until equilibrium was reached. Attainment of equilibrium was judged to have occurred when two or more successive values of the equilibrium constant at any temperature differed by less than 1%. Although time to reach equilibrium varied with temperature from ~18 h at 272 °C to ~2 h at 348 °C, the system was maintained at temperature overnight prior to sampling. Each equilibrium constant presented is the average of 2–4 values generally varying by less than 0.5%. Tetralin and naphthalene were found only in the higher temperature samples (with tetralin accounting for less than 1.3% of the total at 348 °C).

Table I. *cis*-Decalin/*trans*-Decalin Isomerization Equilibria

		mol %			
temp, K	feed	*trans*-decalin	*cis*-decalin	K_e	ln K_e
545	A	89.67	10.33	8.681	2.161
561	A	89.01	10.99	8.099	2.092
575	A	88.30	11.70	7.547	2.021
590	A	87.73	12.27	7.150	1.967
606	A	87.15	12.85	6.782	1.914
621	A	86.49	13.51	6.402	1.857
637	A	85.81	14.19	6.047	1.800
630	B	86.11	13.89	6.199	1.824
568	B	88.73	11.27	7.873	2.064

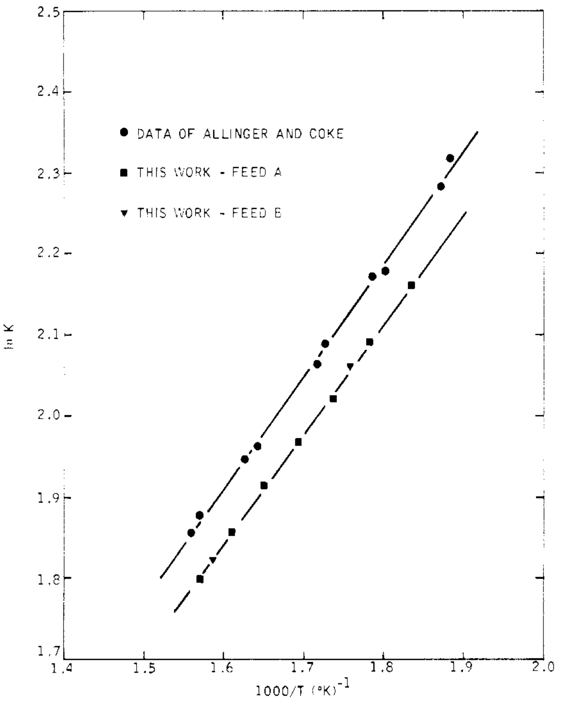

Figure 3. Equilibrium constant plot for the isomerization of *cis*- and *trans*-decalin.

Results

Because of the novel design of the equilibrium cell, experiments to evaluate the accuracy and precision of the results were necessary. The isomerization of *cis*- and *trans*-decalin had been studied previously by Allinger and Coke (*5*) and was selected for this purpose. Temperature and pressure conditions in our study were chosen to be similar. The temperature was varied from 272 (545 K) to 348 °C (621 K) at a constant total pressure of 6.4 MPa and the results are shown in Table I. Equilibrium was approached from both sides by using either pure *trans*-decalin (feed A) or a mixture of 79.5% *trans*-decalin and 20.5% *cis*-decalin (feed B). A plot of the resulting equilibrium constant data and the data of Allinger and Coke is shown in Figure 3.

Linear regression of eq 1 to data from the present work yielded values of −2.75 ± 0.05 kcal/mol and −0.60 ± 0.07 eu for ΔH and ΔS, respectively.

$$\ln K_e = -\Delta H/RT + \Delta S/R \qquad (1)$$

Discussion

Comparison of the equilibrium constants generated in this work with those generated by Allinger and Coke shows that the current values are approximately 10% lower at all temperatures. Yet the enthalpy and entropy of isomerization agree very well with their values of −2.72 ± 0.20 kcal/mol for ΔH and −0.55 ± 0.3 eu for ΔS and with the value of −2.69 ± 0.31 kcal/mol for ΔH measured by Speros and Rossini (*6*). The major reason for the observed differences is believed to be the fact that Allinger and Coke did not actually sample the liquid phase. Instead, they ran a batch reaction for a predetermined length of time and quenched the entire bomb thereby condensing all of the vapor phase into the liquid. They then corrected for this by using estimates of the vapor-phase composition. Systematic errors could have resulted from their extrapolation of the vapor pressure data of Camin and Rossini (*7*) well outside of the measured range and their use of calculated critical parameters.

A second possible source of error lies in the fact that their reaction products were quenched (thermally) in the presence of their catalyst thereby providing the opportunity for some catalytic reaction at lower temperatures resulting in a higher trans/cis ratio.

In the current study, liquid was withdrawn from the reactor at temperature and pressure in the absence of catalyst, thereby requiring no corrections. Since the differences in sampling technique could result in a reasonably constant variation between results from the two studies, almost parallel lines and hence similar values of ΔH would be expected. The small difference in slopes when extrapolated to $(1/T) = 0$ would also explain the similarity in values of ΔS.

Conclusions

The current equilibrium work with *cis*- and *trans*-decalin was done to verify that meaningful thermodynamic data on the hydrogenation of multiring aromatics in the liquid phase could be obtained with a newly designed equilibrium cell. In demonstrating this validity, equilibrium constants which are approximately 10% lower than previously published values were obtained. These differences notwithstanding, the resulting values for the enthalpy and entropy of isomerization were consistent with published values and differences in the values of equilibrium constants can be explained by differences in experimental technique.

Acknowledgment

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Transport Properties of a Long-Chain Molecule with Side Groups Capable of Molecular Orientation. Diffusion of Triolein in *n*-Alkanes at 25 °C

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Measurements of interdiffusion coefficients have been carried out for triolein (glycerol trioleate) in *n*-alkanes at 25 °C. The experimental results are compared to earlier measurements for 1-iododecane in *n*-alkanes, and the discussion is carried out briefly in a qualitative manner.

As a part of research projects at this Institute, extensive measurements of interdiffusion coefficients have been carried out (*1–3*) with the main interest directed toward the influence of the relative size of the solute and solvent molecules on the measured interdiffusion coefficients. The data reported in the present paper mark the end of this type of study.

Experimental Section

Triolein (glycerol trioleate, glycerol tris(*cis*-9-octadecenoate)) was a Fluka reagent-grade chemical. It was used as received.

Table I. Experimental Data for the Diffusion of Triolein in *n*-Alkanes at 25 °C

solvent	$10^7 D_0$, $cm^2\ s^{-1}$	η_0, cP	$10^7 D_0 \eta_0$, dyn	V_m, $cm^3\ mol^{-1}$
n-hexane	88.52	0.2985	0.2642	131.6
n-heptane	69.54	0.3967	0.2759	147.5
n-octane	55.08	0.5151	0.2837	163.5
n-decane	36.79	0.8613	0.3169	195.9
n-undecane	29.00	1.095	0.3176	212.2
n-dodecane	23.35	1.378	0.3218	228.6
n-tridecane	18.45	1.711	0.3157	244.9
n-hexadecane	11.89	3.095	0.3680	294.1
n-heptadecane	9.25	3.711	0.3433	310.5

The *n*-alkanes were the same as those used in previous studies (*1*, *2*).

The method used for the measurements of the diffusion coefficients is that of free diffusion in which an initially sharp boundary is formed between a solution and its pure solvent.

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