obtained on relatively simple systems, indicate quite clearly that a qualitative theory, explaining all of the available experimental facts in this field, cannot yet be established. It is, therefore, futile to generalize results, gathered on few systems, in order to construct a general theory of catalytic action at conducting surfaces. In a general way, the results of this investigation support the idea that the "availability" of electrons for bond formation between the adsorbate and the conducting surface is affected and, therefore, dependent on the electronic characteristics of the latter. This con-

clusion applies whether the chemisorbed bond is covalent, ionic or intermediate in nature. This "availability" may be considered both in terms of energy and entropy, since in all of our samples a linear correlation between the activation energy and the pre-exponential factor obtains.

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# THE NAPHTHALENE-TETRALIN-HYDROGEN EQUILIBRIUM AT ELEVATED TEMPERATURE AND PRESSURE

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The position of the naphthalene-tetralin-hydrogen equilibrium has been determined experimentally at temperatures between 360 and 475° and pressures up to 60 atmospheres. A method of correcting the equilibrium constants for deviations from the ideal gas laws has been devised. The corrected values of  $K_p$  for the hydrogenation of naphthalene can be represented by the relation log  $K_p = -13.13 + 7000/T$ . The calculated heat of hydrogenation of naphthalene at 400° is  $-32.0 \pm 1.2$  kcal./gram mole.

Knowledge of the thermodynamics of the reactions involved in the hydrogen treatment of polycyclic hydrocarbons is very limited. Accurate chemical thermodynamic properties calculated from spectroscopic and third law data are available only for naphthalene<sup>1</sup> and decalins.<sup>2</sup> A semi-empirical calculation of the thermodynamic properties of tetralin also has appeared recently<sup>3</sup> and the results have been used to predict the naphthalene-tetralin equilibrium constant.<sup>4</sup> The naphthalene-tetralin equilibrium was studied experimentally<sup>5</sup> some years ago at low temperatures and pressures, but the results obtained were not of sufficient accuracy to provide a useful check on the calculations. The now reported measurements of the naphthalene-tetralin equilibrium provide an experimental check on the semi-empirical calculations<sup>4</sup> in a region of temperature and pressure of current technical interest. A method of calculating the activity coefficients necessary to convert the experimental results to the ideal gas basis has been devised, and checked with the data obtained.

#### Experimental

The equilibrium measurements were made in an apparatus typical of those employed in the study of catalytic hydrogen treatments of volatile liquid hydrocarbons. The catalyst charge was 150 ml. (0.96 inch i.d. tube) of  $^{1}/_{s}$ -inch pellets of Harshaw molybdena or cobalt molybdate on alumina—either Mo-0201-T or what was thought to be Co-Mo-0401-T. No significant differences between the catalysts were noted. Hydrogen flows varied from 35 to 150 liters per hour and hydrocarbon liquid feed rates from 30 to 300 ml. per hour. Establishment of equilibrium

(1) A. L. McLellan and G. C. Pimentel, J. Chem. Phys., 23, 245 (1955).

- (2) T. Miyazawa and K. S. Pitzer, J. Am. Chem. Soc., 80, 60 (1958).
- (3) A. Székely, Acta Chim. Hung., 5, 317 (1955).
- (4) G. Rabo and A. Székely, ibid., 5, 453 (1955).
- (5) A. Maillard, Ann. combustibles liquides, 10, 95 (1935).

was demonstrated at the higher temperatures by showing the product composition to be independent of the feed rate of tetralin. At the lower temperatures, where minimum feed rates were necessary, establishment of equilibrium was demonstrated by feeding a tetralin-naphthalene mixture of very nearly the equilibrium composition and showing that this composition changed very little, although considerable naphthalene could be formed when tetralin alone was fed.

Liquid products were analyzed on a Perkin-Elmer Vapor Fractometer, Model 154-B. The chromatographic column was packed with 26% Apiezon "N" on "Chromosorb" and operated at 180° with helium as the carrier gas. Calibration with mixtures of the compounds of interest indicated the relative sensitivities<sup>6</sup> (area to weight ratios) to be: naphthalene, 1.00; tetralin 0.945; cis-decalin, 1.09; transdecalin, 0.995.

In most cases analyses were based on areas of peaks identified only by their retention times. In two experiments at  $475^{\circ}$ , where side reactions became important, peaks from the chromatographic column were collected and examined by infrared. For this purpose a  $\frac{3}{4}$  inch o.d. column 2.2 meters long was employed, and the sample size increased to about 2 ml. Separations made with this larger diameter column appeared to be at least as good as those obtained with the standard  $\frac{1}{4}$  inch column. The principal constituent present in a peak appearing at a retention time 76% of that of *trans*-decalin was shown to

The principal constituent present in a peak appearing at a retention time 76% of that of *trans*-decalin was shown to be *n*-butylbenzene. This peak was found in samples from runs at all temperatures investigated. The "*trans*-decalin" peak isolated from samples obtained in runs at 475° was found to contain four or five times as much methylindane as *trans*-decalin.

### **Results and Discussion**

The experimentally determined values of the naphthalene-tetralin equilibrium constants are collected in Table I, with the conditions under which they were measured. These conditions are such that quite substantial deviations from ideal gas behavior are to be expected. The largest deviations should be exhibited by naphthalene and tetra-

(6) These differ slightly from those reported by R. M. Soemantri and H. I. Waterman, J. Inst. Petroleum, 43, 94 (1957).



Fig. 1.—Changes in equilibrium constants with pressure: ⊙, 390° uncor.; ●, 390° cor., ⊡, 450° uncor.; ■, 450° cor.



Fig. 2.—Naphthalene-tetralin-hydrogen equilibrium constants as a function of temperature. Solid line is best empirical representation of data. Dashed line represents calculations of Rabo and Székely.<sup>4</sup>

lin, but only the ratio of these fugacities appears in the equilibrium constant. The activity coefficients of these compounds in the mixture should be very nearly equal, according to the Lewis and Randall rule<sup>7</sup> for the fugacity of mixtures, since their critical temperatures and pressures are very nearly equal. Hence deviations of these two compounds from

(7) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 225-227.

ideality would cancel out in  $K_{\rm p}$ . The presence of the hydrocarbons would, however, be expected to change the behavior of the hydrogen, which otherwise could almost be treated as ideal. The hydrocarbon molecules occupy a portion of the gas phase, and when the finite sizes of hydrogen and hydrocarbon are considered the volume from which the centers of the hydrogen molecules are excluded becomes quite appreciable under the conditions employed.

TABLE I

EXPERIMENTAL DETERMINATIONS OF NAPHTHALENE-TETRA-LIN-Hydrogen Equilibrium

		Pressu	re. atm.	$Meas-ured^a$	Caled. activity coef- ficient.	Cor.ª
Run no.	°C,	Total	Hydro- carbon	$\times$ 104, atm2	hydro- gen	$K_p \times 104$ atm.
99-6	360	14.6	3.54	$89.3^{b}$	1.027	$84.5^{b}$
106-4	360	21.4	5.38	$74.6^{b}$	1.042	$68$ , $4^b$
137-7	390	21.4	3.15	29.0	1.023	27.6
102-4,5	390	35.0	8.5	31.1	1.064	27.3
103-5,6	390.	35.0	10.1	$34.0^{b}$	1.072	$29.6^{b}$
139-5	390	35.0	5.28	26.4	1.042	24.3
141-4	390	35.0	2.83	27.1	1.027	25.7
143-3	390	62.2	4.88	29.2	1.047	26.7
104-6, 123-5	420	48.6	6.4	$10.00^{b}$	1.048	$9.10^{b}$
105-3, 125-9	420	48.6	5.4	9.82	1.043	9.00
110-5,6	450	21.4	2.2	3.45	1.015	3.35
111-3,4	450	41.8	4.3	3.68	1.034	3.44
112-8	450	41.8	4.3	3.90	1.034	3.65
108-4,6,10	450	62.2	7.3	3.80	1.053	3.41
135-4,10	475	35.0	3.4	2.06	1.024	1.96
113-6	475	62.2	7.68	1.94	1.056	1.74
114-5,6,7	475	62.2	6.9	2.10	1.053	1.89
145-5	475	62.2	3.6	2.01	1.033	1.88

 $^{a}K_{\rm p} = (N_{\rm CloH_{12}}/N_{\rm CloH_{8}}N^{2}_{\rm H_{2}}) \times 1/P^{2}$ , where  $N_{\rm i}$  = mole fraction of component i in the gas, P = the total pressure in atmospheres.  $K_{\rm p}$  (corrected) =  $K_{\rm p}/\gamma^{2}_{\rm H_{2}}$ . <sup>b</sup> Feed contained 35% naphthalene, 65% tetralin by weight.

The excluded volume can be calculated in a manner similar to that employed<sup>8</sup> to evaluate the b term in the van der Waals equation for a single gas. It is only necessary to consider that all the hydrocarbon is present as isolated molecules when the hydrogen is added. If the diameter of a hydrogen molecule is taken to be 2.8 Å., and the hydrocarbon molecules are assumed to be discs 3 Å. thick and 9 Å, in diameter, the excluded volume is calculated to be about three times the actual volume of the hydrocarbon-assuming the hydrocarbon to have a density of 1.145 (naphthalene). This quantity was added to the b, 0.015 liter per mole, found empirically for hydrogen alone in the appropriate temperature range. The *a* term in the van der Waals equation of state for hydrogen was presumed to remain negligible in comparison to b. Values of the activity coefficient calculated in the above manner are shown in Table I.

Measurements of  $K_p$  were made over a range of total pressures and hydrocarbon partial pressures. These provide material with which to test the validity of the arguments presented concerning fugacities. It will be assumed that the calculated activity coefficients provide the best available measure

(8) S. Glasstone, "Textbook of Physical Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1954, p. 294, of the relative tendencies of particular reaction conditions to produce deviations from ideal gas behavior. If, then, the observed values of  $K_p$  are plotted against the calculated activity coefficients, the points should fall on a line whose deviation from the horizontal provides a measure of the deviation of the system from ideality. The data obtained at 390 and 450° are plotted in this manner in Fig. 1. The corrected values of  $K_p$  are shown in the same figure for comparison. Within the rather large uncertainty in the experimental data, the calculated corrections can be said to be of the right magnitude. The corrected values therefore will be employed to characterize the equilibria.

characterize the equilibria. The corrected  $K_p$ 's for the naphthalene-tetralin equilibrium shown in Table I were fitted by least squares to an Arrhenius-type equation. The result is

$$\log K_{\rm p} = -13.13 + \frac{7000}{m} \tag{1}$$

where  $K_{\rm p}$  is in (atmospheres)<sup>-2</sup> and T in degrees Kelvin. The standard deviation of individua points from this line is  $\pm 15\%$ , the worst offender being the lowest temperature point where attainment of equilibrium was relatively uncertain. From the constants given,  $\Delta H^{0}_{400} = -32.0 \pm 1.2$ kcal./g. mole and  $\Delta S^{0}_{400} = -60.1$  cal./deg. mole. The uncertainty given for  $\Delta H^{0}_{400}$  represents the 0.95 confidence limit calculated statistically from the experimental data. If a value of  $\Delta H^{0}_{400}$  were determined accurately by some other means, the measurements of  $K_{0\rm p}$  would serve to define  $\Delta S^{0}_{400}$  to  $\pm 0.2$  cal./deg. mole. The equation given can be compared with that of Rabo and Székely<sup>4</sup>

$$\log K_{\rm p} = -13.65 + \frac{7350}{T} \tag{2}$$

Between 390 and  $450^{\circ}$  the differences in the two constants compensate and both equations fit the experimental data very well. This is shown in Fig. 2.The difference in the slopes of the two lines, while not very great, is still outside the calculated 0.95 confidence limits. At 475° the average of seven individual experimental determinations of the equilibrium constant would have to be too high by more than 20% if Rabo and Székely's calculations are correct. Until the purity of the materials separating into chromatographic peaks was determined it appeared possible that side reactions at the high temperature might lead to products which would interfere in the chromatographic analysis. Both the naphthalene and tetralin peaks proved, however, to be more than 95% the expected material, with the principal contamination of the tetralin being naphthalene-the nearest major con-stituent of the mixture. It, seems probable therefore, that equation 1 represents a significant improvement over equation 2 as a representation of the effect of temperature on the value of the naphthalene-tetralin-hydrogen equilibrium constant at temperatures between 350 and 500°.

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# THE SOLUBILITY OF CIS- AND TRANS-DINITROTETRAMMINE-COBALT-(III) IODATE AND CIS- AND TRANS-DINITROTETRAMMINE-COBALT(III) dl-DINITROÖXALATODIAMMINE COBALTATE IN DIOXANE-WATER, ETHANOL-WATER AND ACETONE-WATER MIXED SOLVENTS AT 15 AND 25°

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The solubilities of the iodate and the *dl*-dinitroöxalatodiammine cobaltate of the two cations *cis*- and *trans*-dinitrotetrammine-cobalt(III) have been determined in dioxane-water, ethanol-water and acetone-water mixtures at 15 and 25°. Values of  $\Delta H^0$ ,  $\Delta F^0$  and  $\Delta S^0$  for the solution process have been calculated.

This paper reports the results of a study of the change of solubility of the iodates and *dl*-dinitrooxalatodiammine cobaltates of *cis*- and *trans*dinitrotetrammine-cobalt(III) with change in the dielectric constant of the solvent. The dielectric constant was changed by adding dioxane, ethanol or acetone to water. These salts were chosen because they are relatively insoluble, yet their concentrations can be determined accurately by analysis for ammonia. The comparison of the solubility of the *cis*-trans pair may help to determine which forces are important in the solution process.

### Experimental

The cobaltammine complex ions were prepared by methods previously described.<sup>1</sup> The cobaltammine anion was obtained as ammonium *dl-cis*dinitroöxalato-*cis*-diammine cobaltate by careful recrystallization.<sup>2</sup> The salts for solubility studies were formed by precipitation and purified by shaking with successive portions of water until a con-

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