[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Thermodynamic Functions for Gaseous *cis*- and *trans*-Decalins from 298 to 1000°K.[1]

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The values of the heat content function, free energy function, heat capacity and entropy of *cis*- and *trans*-decalins have been calculated by the use of molecular and thermal data. The functions are tabulated from 298 to 1000°K. The heat, free energy and equilibrium constants of the reactions, $C_{10}H_8 + 5H_2 = cis\text{-}C_{10}H_{18}$, $C_{10}H_8 + 5H_2 = trans\text{-}C_{10}H_{18}$, have been also calculated and tabulated.

Experimental thermodynamic data are available for liquid *cis*- and *trans*-decalins. It was our purpose to calculate functions for the gaseous state over a range of temperature. In either case the data for the heat capacity and entropy of the liquid[2] at temperatures up to 350°K. and precise vapor pressure measurements[3] in the range 370–460°K. are available. Therefore, a short extrapolation must be made if one is to obtain thermodynamic functions for these substances in the gaseous state in the range 400–450°K. In the absence of other information, the equations for the heat capacity of the liquid as a function of temperature were obtained by best fitting a straight line to the experimental values available in the range 300–350°K. The equations are

$$C_p = 12.68 + 0.1434T \ (cis\text{-decalin}) \qquad (1)$$

$$C_p = 10.95 + 0.1464T \ (trans\text{-decalin}) \qquad (2)$$

These equations were used for the extrapolation of the liquid heat capacity and the calculation of the entropy of the liquid in the range 400–450°K.

The values of the heat capacity and entropy of vaporization at several temperatures were calculated from the vapor pressure equations of Camin and Rossini[3] on the assumption that the vapor volume follows the Berthelot equation of state with critical constants T_c = 691.7°K. and P_c = 27 atm. for *cis*-decalin and T_c = 681.5°K. and P_c = 27 atm. for *trans*-decalin.[4] The correction of the heat capacity and entropy to the ideal gas state was made with the aid of the Berthelot equation, and the entropy of compression was then added. The heat capacity and entropy values for the ideal gases at the standard pressure of one atmosphere are shown in Tables I and II.

The contribution of the molecular rotation to the entropy was calculated by using the bond distances 1.54 and 1.09 Å. for C–C and C–H bond, respectively, and tetrahedral angles for all the bond angles. The symmetry number for either case is two; however, in the case of *cis*-decalin $R \ln 2$ = 1.38 cal./deg. mole must be added on account of the presence of two equivalent inversion isomers (or conformations). The contributions of molecular vibration to the heat capacity and entropy of *cis*-decalin were calculated by the use of the observed infrared[5] and Raman[6] frequencies. Those are: 2890(18),[7] 1444(8),[7] 1384, 1350, 1342, 1327, 1312, 1300, 1292, 1270, 1258, 1241, 1216, 1210, 1171, 1165, 1143, 1125, 1114, 1089, 1073, 1069, 1041, 1011, 978, 969, 929, 888, 877, 849, 855, 835, 800, 793, 752, 742, 706, 661, 594, 538, 489, 446, 375, 348, 317, 191 and 148. In addition to the incompletely resolved groups of frequencies near 2900 and 1450 cm.$^{-1}$, there are seven unobserved vibrations of lower frequency. The contributions of these unobserved fundamentals to the heat capacity and entropy were calculated by subtracting the contributions of translation, rotation and observed vibrations from the thermal values of heat capacity and entropy at 400°K., and were found to be 5.88 and 7.10 cal./deg. mole, respectively. It was found that these values may be explained by assuming the presence of two fundamentals near 150 cm.$^{-1}$ and five fundamentals near 1300

TABLE I

CALCULATION OF THE ENTROPY OF *cis*- AND *trans*-DECALINS (IN CAL./DEG. MOLE)

	cis-Decalin		*trans*-Decalin	
Temp., °K.	400	450	400	450
Entropy of liquid	81.67	90.34	81.43	90.04
Vaporization	26.44	21.88	25.43	21.01
Gas imperfection	0.05	0.14	0.06	0.17
Compression to 1 atm.	−3.82	−0.91	−3.30	−0.50
Entropy (3rd law)	104.34	111.45	103.62	110.72
Trans. and rot.	72.27	73.20	71.12	72.06
Vibration	32.05	38.29	32.49	38.71
Entropy (calcd.)	104.32	111.49	103.61	110.77

TABLE II

CALCULATION OF THE HEAT CAPACITY OF *cis*- AND *trans*-DECALINS (IN CAL./DEG. MOLE)

	cis-Decalin		*trans*-Decalin	
Temp., °K.	400	450	400	450
Heat capacity (liq.)	70.04	77.21	69.51	76.83
Vaporization	−13.59	−12.63	−12.92	−12.26
Gas imperfection	0.14	0.43	0.18	0.51
Heat capacity (gas, exp.)	56.59	65.01	56.77	65.08
Trans. and rot.	7.95	7.95	7.95	7.95
Vibration	48.68	56.56	48.83	56.65
Heat capacity (gas, calcd.)	56.63	64.51	56.78	64.60

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[1] This research was part of the program of Research Project 50 of the American Petroleum Institute.

[2] Private communication from Dr. G. Waddington, U. S. Bureau of Mines, Bartlesville, Oklahoma.

[3] D. L. Camin and F. D. Rossini, *J. Phys. Chem.*, **59**, 1173 (1955).

[4] Kamez, Gross, Trappe, quoted by L. Riedel, *Chem. Ing. Tech.*, **24**, 353 (1954).

[5] American Petroleum Institute Research Project 44, Infrared Spectra Data, Serial No. 1086 and 1087.

[6] Landolt-Börnstein, "Zahlenwerte und Funktionen," I Band, 2 Teil, Berlin, 1951, p. 502.

[7] The value is the average of the observed frequencies. There are eighteen CH stretching and eight CH_2 bending vibrations.

TABLE III

CALCULATED VALUES OF THERMODYNAMIC PROPERTIES OF *cis*- AND *trans*-DECALINS IN THE IDEAL GAS STATE (IN CAL./DEG. MOLE)

	cis-Decalin				*trans*-Decalin			
T, °K.	Cp^0	$\frac{H^0 - H_0^0}{T}$	$-\frac{(F^0 - H_0^0)}{T}$	S^0	Cp^0	$\frac{H^0 - H_0^0}{T}$	$-\frac{(F^0 - H_0^0)}{T}$	S^0
298.16	39.84	20.55	69.73	90.28	40.04	20.75	68.77	89.52
300	40.14	20.67	69.84	90.51	40.36	20.89	68.86	89.75
400	56.64	27.64	76.68	104.32	56.78	27.84	75.78	103.62
500	71.64	35.02	83.70	118.71	71.14	35.17	82.83	118.01
600	84.14	42.17	90.65	132.82	84.20	42.35	89.79	132.14
700	94.71	48.93	97.69	146.62	94.77	49.09	96.87	145.96
800	103.36	55.17	104.64	159.82	103.40	55.29	103.85	159.14
900	110.65	60.95	111.46	172.41	110.67	61.07	110.68	171.74
1000	116.91	66.23	118.14	184.37	116.93	66.35	117.36	183.71

TABLE IV

HEAT (ΔH^0) AND FREE ENERGY (ΔF^0) (IN KCAL./MOLE) AND EQUILIBRIUM CONSTANT (K) OF REACTIONS

	$C_{10}H_8 + 5H_2 = cis\text{-}C_{10}H_{18}$			$C_{10}H_8 + 5H_2 = trans\text{-}C_{10}H_{18}$		
T, °K.	ΔH^0	$-\Delta F^0$	log K	ΔH^0	$-\Delta F^0$	log K
298.16	−76.71	+33.12	+24.27	−79.90	+36.08	+26.44
300	−76.76	+32.84	+23.92	−79.94	+35.80	+26.08
400	−79.17	+17.81	+ 9.73	−82.34	+20.70	+11.31
500	−81.01	+ 2.28	+ 0.99	−84.18	+ 5.09	+ 2.22
600	−82.34	−13.63	− 4.97	−85.48	−10.90	− 3.97
700	−83.21	−29.70	− 9.28	−86.35	−27.02	− 8.44
800	−83.72	−45.85	−12.53	−86.87	−43.23	−11.81
900	−83.86	−62.08	−15.07	−87.00	−59.53	−14.45
1000	−83.77	−78.32	−17.12	−86.90	−75.85	−16.58

	$C_{10}H_8 + 5H_2 = \text{equil. } C_{10}H_{18}$			$trans\text{-}C_{10}H_{18} = cis\text{-}C_{10}H_{18}$			
T, °K.	ΔH^0	$-\Delta F^0$	log K	ΔH^0	$-\Delta F^0$	K	% *cis* at equil.
298.16	−79.88	+36.08	+26.44	+ 3.19	− 2.96	0.007	0.7
300	−79.92	+35.80	+26.08	+ 3.18	− 2.96	.007	0.7
400	−82.26	+20.72	+11.32	+ 3.17	− 2.89	.026	2.5
500	−84.01	+ 5.14	+ 2.24	+ 3.17	− 2.81	.056	5.3
600	−85.19	−10.78	− 3.93	+ 3.14	− 2.73	.102	9.3
700	−85.95	−26.83	− 8.38	+ 3.14	− 2.68	.145	12.7
800	−86.37	−42.95	−11.73	+ 3.15	− 2.62	.191	16.0
900	−86.39	−59.15	−14.36	+ 3.14	− 2.55	.240	19.4
1000	−86.20	−75.35	−16.47	+ 3.13	− 2.47	.288	22.4

cm.$^{-1}$. These numbers of fundamentals assigned for each region may be understood if we consider the expected numbers of fundamentals and also the possibility of overlapping of CH bending vibrations. By the use of the observed as well as the assumed fundamental frequencies, the values of the heat capacity and entropy of *cis*-decalin at 450°K. are calculated and shown in Tables I and II. The agreement between the thermal and molecular values is quite satisfactory.

In the case of *trans*-decalin A_u and B_u fundamentals in the low frequency region have not been observed. The contribution of these fundamentals to the value of the entropy and heat capacity is substantial. Fourteen fundamentals are unobserved, and it is not meaningful to select individual frequencies and obtain agreement between the thermal and molecular values. However, most of the fundamental frequencies of *trans*-decalin must be closely similar to the corresponding modes for the *cis*-isomer. Only the very low skeletal bending frequencies would be expected to differ substantially in the two cases. Consequently, we made a minimum adjustment in the *cis* frequencies in order to fit the entropy and heat capacity of the *trans*-isomer at 400°K. This comprised a shift of the single frequency at 446 to 350 cm.$^{-1}$. This assignment also yielded agreement between the thermal and molecular values at 450°K. as shown in Tables I and II.

By the use of molecular data, including the aforementioned vibrational frequencies, the heat capacity, heat content, entropy and free energy of *cis*- and *trans*-decalins were calculated and are listed in Table III.

The standard heats of formation at 298.16°K. are −52.45 ± 0.22 kcal./mole for liquid *cis*-decalin and −55.14 ± 0.22 kcal./mole for liquid *trans*-decalin.[8] The value for solid naphthalene[8] is 18.75 ± 0.38 kcal./mole. The standard heat of formation in the ideal gas state was then obtained by adding to the heat of formation in the condensed state, the heat of vaporization, which was calculated from the difference between the entropy in the ideal gas state and that of the condensed state. The values of the standard heat of formation in the ideal gas state are +36.33 kcal./mole for naphthalene, −40.38 kcal./mole for *cis*-decalin, and −43.57 kcal./mole for *trans*-decalin. Using these values,

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(8) Private communication from Dr. F. D. Rossini, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

and the heat content, and free energy functions of hydrogen,[9] naphthalene[10] and *cis*- and *trans*-decalins, the heat, free energy and equilibrium constants of various decalin reactions have been calculated as shown in Table IV. We did not find any published values of experimental measurements of these equilibria for comparison with our results.

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[9] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

[10] A. L. McClellan and G. C. Pimentel, *J. Chem. Phys.*, **23**, 245 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Reaction Kinetics by the Matrix Isolation Method: Diffusion in Argon; *cis–trans* Isomerization of Nitrous Acid

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The use of the matrix isolation technique for the study of reaction rates of chemical reactions with heats of activation as low as one or two kcal. is described. Reactions which might be studied include isomerization, bond rupture, bond formation reactions and the process of diffusion in the solid matrix. A crude estimate of the rate of diffusion of ammonia in solid argon is presented. The heat of activation of the isomerization of *cis*-HNO_2 to *trans*-HNO_2 was measured at 20°K. in solid nitrogen and found to be much lower than current estimates.

The matrix isolation method, as proposed by Whittle, Dows and Pimentel,[1] involves the deliberate suspension of reactive molecules in a rigid and inert solid matrix for the purpose of spectroscopic study of these molecules. It is the purpose of this paper to note that the technique not only provides a means of keeping reactive molecules apart but also a method of bringing them *together* under unusual environmental conditions. In particular, two reactive molecules can be formed together (*e.g.*, by photolysis) or brought together (*e.g.*, by diffusion in the solid) at extremely low temperatures where measurable reaction rates will be observed even for free energies of activation of the order of one or two kilocalories, a range relatively inaccessible to measurement by other methods. In this paper the experimental technique is described, examples are cited, and difficulties of interpretation are discussed.

Proposed Experimental Procedure.—In this Laboratory, the process of diffusion of a molecule A suspended in a matrix M[2] has been studied. The temperature at which such a diffusion process becomes rapid seems to be around three to five tenths of the melting point of the pure matrix. Thus a molecule such as NO_2, H_2O or NH_3 diffuses rapidly in solid argon (T_m = 83.8°K.) at temperatures above 35°K. Hence reactive molecules can be brought together in solid argon in a period of a few seconds at 40–50°K. and thereafter their fates can be studied spectroscopically as a function of time. Other matrix materials can be used to obtain either higher or lower diffusional temperatures.

Reaction Processes in the Matrix.—Of the possible reactions which might take place under the proposed conditions, the simplest type would be the first-order deactivation of an excited state, *e.g.*, a state involving conformational or tautomeric excitation. In the former case, the rate of formation of the most stable isomer would be determined by the potential function which governs the intramolecular movement, for example, a potential barrier hindering internal rotation. (Entropy effects will be discussed later.) In the case of tautomers, the process would be governed by the properties of the transition state in intramolecular rearrangement. If the confines of the matrix impede intramolecular movements, the measured heat of activation probably will exceed that of the gaseous molecule.

Bond rupture reactions would also be of first order. The effect of the matrix cage on $\Delta H^{\ddagger}$ would depend upon the dimension along the reaction coördinate of the activated state, $r^{\ddagger}_{AB}$, compared to the size of the matrix cage. If the cage is small compared to $r^{\ddagger}_{AB}$, then $\Delta H^{\ddagger}$ will be influenced by the heat of activation of diffusion, $\Delta H^{\ddagger}_{D}$, the heat of activation for reaction in the gas phase, $\Delta H^{\ddagger}_{0}$, and the heat of reaction, ΔH_R. Situations which are readily interpreted are the special cases: (1) $\Delta H^{\ddagger} >> \Delta H^{\ddagger}_{D}$; (2) $\Delta H^{\ddagger}_{D} >> \Delta H^{\ddagger}_{0}$ and $r^{\ddagger}_{AB}$ comparable to the cage size; and (3) of $r^{\ddagger}_{AB}$ small compared to the cage size. In case (1) the value of $\Delta H^{\ddagger}$ measured is little influenced by the matrix and in case (2) the measured $\Delta H^{\ddagger}$ is approximately $\Delta H^{\ddagger}_{D}$. In case (3) the potential curve applicable to the gas phase, curve a in Fig. 1, may be influenced somewhat by the matrix cage, as suggested by curves b and c in Fig. 1. Again the measured activation enthalpy should exceed the gas phase $\Delta H^{\ddagger}_{0}$.

Reactions involving bond formation are also influenced by cage size. However, in either case (1) or (2) the reaction kinetics become of second order. In case (3) it is possible for the reaction to occur within the cage and at a temperature at which diffusion cannot take place. If a potential curve such as curve b of Fig. 2 were applicable, the kinetics would be first order because the reactive species are held together by the matrix. In a favorable case, where the cage is very large compared to $r^{\ddagger}_{AB}$, $\Delta H^{\ddagger}$ would provide an estimate of $\Delta H^{\ddagger}_{0}$.

A fourth type of reaction, diffusion, can be studied. The rate can be determined by observing the disappearance of a suitable suspended species which reacts with low $\Delta F^{\ddagger}$.

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[1] E. Whittle, D. A. Dows and G. C. Pimentel, *J. Chem. Phys.*, **22**, 1943 (1954).

[2] E. D. Becker and G. C. Pimentel, *ibid.*, **25**, 224 (1956).