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RECEIVED for review October 24, 1962. Accepted February 25, 1963.

Heat and Free Energy of Formation of the *Cis*- and *Trans*-Decalins, Naphthalene and Tetralin from 298° to 1000° K.

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Values of the heat (ΔH_f°) and free energy (ΔF_f°) and $\log_{10}$ of the equilibrium constant of formation (K_f) are calculated for the *cis*- and *trans*-decalins, naphthalene, and tetralin in the ideal gas state from 298° to 1000° K. from thermodynamic data.

VALUES for the free energy of formation of tetralin in the gaseous state are calculated by combining published thermodynamic data on napthalene and published measurements of the equilibrium in the hydrogenation of naphthalene to tetralin. Because no values for the free energy of formation of either naphthalene or decalin were found in the literature, they are also included in Table I.

The heat and free energy of formation of the *cis*- and *trans*-decalins from 298.16° to 1000° K. were calculated from the heat content and free energy functions of hydrogen (*8*), carbon (*8*), and the *cis*- and *trans*-decalins (*7*), and the measured heats of formation of the *cis*- and *trans*-decalins (*9*) at 298.16° K.

The heat and free energy of formation of naphthalene were calculated similarly from the heat content and free energy functions of naphthalene (*4*) and the measured heat of formation of naphthalene (*9*) at 298.16° K. The heat and free energy values at 298.16° K. agree with those published recently by Miller (*6*); however, the values for the free energy of formation at higher temperatures in the latter paper are in error. (In a private letter Miller's corrected values at 400 and 500° K. agree with those in Table I.).

The thermodynamic data for tetralin in the ideal gas state for the temperature range 298° to 1000° K. were obtained as follows:

1. Values of the heat capacity of the liquid in the temperature range 320° to 480° K. were obtained by extrapolation of the heat capacity data in the 250 to 320° K. range given by McCullough, *et al.*, (*5*). The entropy values of the liquid were obtained by integration of the equation (least squares fit) representing the heat capacity as a function of temperature.
2. Values of the entropy of vaporization at several temperatures were calculated from vapor pressure data given by Mair and Streiff (*3*). The following Antoine equation was found to represent their three measurements of the vapor pressure.

$$\log_{10} P_{\text{mm}} = 6.98280 - \frac{1667.693}{198.987 + t^\circ \text{ C.}}$$

It was assumed that the vapor volume follows the Berthelot equation of state with critical constants T_c = 719.2° K. and P_c = 34.67 atm. (*1*). The Berthelot equation was used, also, in the correction of the entropy to the ideal gas state.

Table I. Heat (ΔH_f°) and Free Energy (ΔF_f°) (in Kcal./Mole) and Log_{10} of the Equilibrium Constant of Formation (K_f) in the Ideal Gas State (Entropy of Tetralin, Cal./Deg. Mole)

	Trans-Decalin			*Cis*-Decalin		
T° K.	ΔH_f°	ΔF_f°	$\text{Log}_{10} K_f$	ΔH_f°	ΔF_f°	$\text{Log}_{10} K_f$
298.16	–43.54	17.58	–12.88	–40.45	20.44	–14.98
300	–43.61	17.97	–13.09	–40.53	20.82	–15.17
400	–47.47	39.10	–21.36	–44.40	41.90	–22.89
500	–50.49	61.09	–26.70	–47.42	63.81	–27.89
600	–52.73	83.68	–30.48	–49.69	86.32	–31.44
700	–54.34	106.53	–33.26	–51.30	109.12	–34.07
800	–55.42	129.55	–35.39	–52.37	132.08	–36.08
900	–55.96	152.74	–37.09	–52.92	155.21	–37.69
1000	–56.09	175.98	–38.46	–53.06	178.36	–38.98

	Naphthalene			Tetralin[a]			
T° K.	ΔH_f°	ΔF_f°	$\text{Log}_{10} K_f$	ΔH_f°	ΔF_f°	$\text{Log}_{10} K_f$	S°
298.16	36.25	53.55	–39.25	(6.65)	(40.38)	(–29.60)	87.7
300	36.22	53.66	–39.09	(6.60)	(40.59)	(–29.57)	88.0
400	34.76	59.70	–32.62	(4.52)	(52.26)	(–28.55)	100.9
500	33.58	66.07	–28.88	(3.01)	(64.37)	(–28.14)	114.0
600	32.64	72.67	–26.47	1.62	76.77	–27.96	126.0
700	31.90	79.40	–24.79	–0.13	89.43	–27.92	136.3
800	31.34	86.24	–23.56	–2.71	102.39	–27.97	144.7
900	30.93	93.11	–22.61	(–6.59)	(115.74)	(–28.11)	150.9
1000	30.70	100.02	–21.86	(–12.24)	(129.62)	(–28.32)	154.8

[a] Values of ΔF_f° and $\text{Lob}_{10}K_f$ below 600° K. and above 800° K. are known less accurately because the extent of extrapolation is greater.

Table II. Calculation of the Entropy of Tetralin in the Ideal Gas State (in Cal./Deg. Mole)

Temperature, ° K.	393.37	433.13	480.73
Entropy of liquid	76.01	82.41	89.98
Vaporization	29.30	25.27	21.36
Gas Imperfection	0.02	0.06	0.16
Compression to 1 atm.	–5.14	–2.49	0.0
Entropy of gas	100.19	105.25	111.50

3. The entropy calculations for the ideal gas at one atmosphere are summarized in Table II for the three temperatures at which the vapor pressure was measured.

4. Values of the entropy of the gas were plotted as a function of temperature and values of the entropy of formation of the gas at 300°, 400°, and 500° K. were obtained by combination with the entropies of carbon (*8*) and hydrogen (*8*).

5. A value for the entropy of formation of tetralin gas at 700° K. (–127.9 cal./deg. mole) was evaluated by combining the (a) free energy of formation of naphthalene and the measured value of the equilibria for the hydrogenation of naphthalene to tetralin (*10*).

$$\log_{10} K = -13.13 + \frac{7000}{T} \text{ (in the temperature range 630°–745° K.)}$$

and (b) the heat of formation of naphthalene at 700° K. and the heat of hydrogenation of naphthalene to tetralin (–32.0 kcal./mole) (*10*). Recent measurements of the naphthalene-tetralin-decalin equilibria (*2*) (in the temperature range 616° to 702° K.) agree with those of Wilson, *et al.*, and with the equilibria calculated by Miyazawa and Pitzer.

6. The values of the entropy of formation at 300°, 400°, 500°, and 700° K. were used to obtain the following equation for tetralin gas.

$$\Delta S_f^\circ = -179.980 \log_{10} T + 0.24667T - 0.00011773T^2 + 269.13$$

7. An equation for ΔH_f° as a function of temperature was obtained from the constants in the above equation and the value of $\Delta H_f^\circ = -130$ cal./mole at 700° K. (*10*).

$$\Delta H_f^\circ = 21{,}070 - 78.164T + 0.123336T^2 - 0.000078485T^3$$

8. An equation for ΔF_f° as a function of temperature was obtained from a combination of the above two equations.

$$\Delta F_f^\circ = 21{,}070 - 347.294T + 179.980T \log_{10} T - 0.123334T^2 + 3.9245 \times 10^{-5} T^3$$

No values for the heat of combustion of tetralin have been reported; therefore no confirmation of the calculated values can be made at this time.

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RECEIVED for review April 24, 1963. Accepted July 24, 1963.