v = molar volume, cc./gram-mole
v_c = critical volume, cc./gram-mole
z_c = critical compressibility factor, $P_c v_c / RT_c$

Greek

D = self-diffusivity, sq. cm./sec.
μ = viscosity, g./cm. sec.
μ^* = viscosity at atmospheric pressure, g./cm. sec.
π = constant, 3.14159
ρ = density, g./cc.
ρ_c = critical density, g./cc.
ρ_R = reduced density, ρ/ρ_c
σ = collision diameter, cm.
χ = probability of nearness

LITERATURE CITED

(1) Enskog, David, *Svensk. Vetenskapsakad. Handl.* **63**, No. 4 (1922).
(2) Hamrin, C.E., Jr., Ph.D. dissertation, Northwestern University, Evanston, Ill., 1964.
(3) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," Wiley, New York, 1954.
(4) Michels, A., DeGraff, W., Wassenaar, T., Levelt, J.M.H., and Louwerse, P., *Physica* **25**, 25 (1959).
(5) Rice, S.A., Kirkwood, G., Ross, John, Zwanzig. R.W., *J. Chem. Phys.* **31**, 575 (1959).
(6) Schaefer, C.A., Thodos, George, *A.I.Ch.E. J.* **5**, 155 (1959).
(7) Snider, R.F., Curtiss, C.F., *Phys. Fluids* **1**, 122 (1958).

RECEIVED for review December 13, 1965. Accepted May 9, 1966.

Thermodynamic Properties of Uranium Carbides via the U-C-O System

JAMES M. LEITNAKER and T. GORDON GODFREY
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

Equilibrium data of Piazza and Sinnott in the systems UO_2-"UC_2"-C-CO and UO_2-"UC_2"-UC-CO have been recalculated using both second and third law treatments. Internal consistency is excellent for the first system and acceptable for the second. Third law treatments predict the heats of formation, ΔH°_{298}, "UC_2" and UC to be −20.5 and −23.2 kcal. per mole, respectively, in excellent agreement with combustion measurements. The "best" value of $\Delta H^\circ_{f,298}$ "UC_2" is −20.8° 0.7 kcal. per mole.

THE influence of oxygen on uranium dicarbide could be important in reactor technology. A panel assembled in Vienna in 1962 by the International Atomic Energy Agency (*7*) assumed the existence of an "oxygen-stabilized uranium dicarbide," UC_xO_y. It has been estimated that the free energy of formation of oxygen-saturated "UC_2" is about 5 kcal. more negative than that of the pure dicarbide (*7, 15*), from which arises the term "oxygen-stabilized."

Piazza and Sinnott studied equilibria in the system UO_2-"UC_2"-C-CO by measuring CO partial pressures (*14*). For their stated reaction

$$UO_2 + 4C = UC_2 + 2CO \qquad (1)$$

Piazza and Sinnott reported

$$\Delta F^\circ_T = 164{,}500 - 74.23\ T \pm 1200 \text{ cal. per gram-mole} \qquad (2)$$

over the range 1714° to 1922° K. The Vienna Panel stated that "the derived heats and entropies are rather unreasonable." This note points out that auxiliary thermal data are now available to treat these measurements of Piazza and Sinnott in the usual fashion; that the internal consistency of these data is excellent; that reasonable heats and entropies are obtained; and that the data, combined with other information, predict that any stabilization by oxygen must be less than a few hundred calories. We also treat data on the UO_2-"UC_2"-UC-CO system by the same authors (*14*).

Two methods are customarily used to treat data of the type obtained by Piazza and Sinnott: the second law slope-intercept treatment and the third law method which involves the use of free energy functions (*9*). We have used these standard methods and the CO partial pressures of Piazza and Sinnott to treat the reaction

$$UO_2 + 3.86C = UC_{1.86} + 2CO \qquad (3)$$

Following Piazza and Sinnott, we estimated the activity of $UC_{1.86}$ to be 0.95 in all experiments they performed and a_{UO_2} and a_C to be unity. Auxiliary data have been obtained as follows. Uranium oxide thermal functions were calculated from the data of Conway and Hein (*1*) combined with the data of Moore and Kelly (*13*). The heat of formation of UO_2, $\Delta H^\circ_{f,298}$, was taken to be −259.0 kcal. per mole from the compilation of Rand and Kubaschewski (*16*). All data on CO were taken from the JANAF tables (2). Data for C (graphite) were taken from the compilation of Stull and Sinke (*17*). Thermal functions for $UC_{1.86}$ were calculated from the data of Levinson (*12*). The low-temperature C_p data of Jones, Gordon, and Long (*8*) were used for UO_2. The data of Westrum *et al.* (*3, 18*) were used for $UC_{1.86}$ with a small (and insignificant) correction for composition plus a configuration entropy term.

For the second law treatment of Reaction 3 an average ΔC_p of 1.0 cal. °K^{-1} was computed over the temperature range 1700° to 2000° K. The resulting equation calculated was

$$\Delta F^\circ = 182{,}300 - 1.0\ T \ln T - 77.1\ T \text{ cal.} \qquad (4)$$

an equation which is cast in the form

$$\Delta F^\circ = \Delta H^\circ_{1800} - 1800(\overline{\Delta C}_p) - \overline{\Delta C}_p\ T \ln T + IT \qquad (5)$$

where I is the computed intercept (*9*). We suggest that Piazza and Sinnott made a numerical error in computing the least squares slope and intercept; our calculated line fits their data better. The internal consistency of the data for Reaction 3 is excellent, much better than might be expected considering the narrow temperature range and small number of measurements, as demonstrated by the following:

Table I. Calculated Thermodynamic Functions

Temp., °K.	Free Energy Functions, $(F^\circ_T - H^\circ_{298})/T$, Cal. °K.$^{-1}$ G.-Mole^{-1}			Heat Capacities, C°_p, Cal. °K.$^{-1}$ G.-Mole^{-1}			Entropies, S°_T, Cal. °K.$^{-1}$ G.-Mole^{-1}			Heat Contents, $H^\circ_T - H^\circ_{298}$, Kcal. G.-Mole^{-1}		
	UO_2	$UC_{1.86}$[a]	UC	UO_2	$UC_{1.86}$	UC	UO_2	$UC_{1.86}$[a]	UC	UO_2	$UC_{1.86}$	UC
1700	−35.62	32.98	−27.20	21.95	29.1	15.42	52.14	49.52	39.40	28.090	28.127	20.739
1800	−36.57	33.94	−27.90	22.15	29.1	15.45	53.40	51.19	40.28	30.295	31.038	22.282
1900	−37.49	34.89	−28.58	22.35	29.1	15.49	54.60	52.76	41.12	32.519	33.948	23.829
2000	−38.37	35.82	−29.23	22.54	29.1	19.57	55.75	54.26	42.06	34.764	36.858	25.674

[a] Contribution to entropy of 0.601 e.u. added to take into account random orientation of carbon vacancies.

$$\Delta H^\circ_{298}\ (2nd) = 187.9 \pm 8.0\ \text{kcal.} \quad (6)$$

$$\Delta H^\circ_{298}\ (3rd) = 185.5 \pm 0.24\ \text{kcal.} \quad (7)$$

$$\Delta S^\circ_{1800}\ (2nd) = 85.6 \pm 4.3\ \text{cal. deg.}^{-1} \quad (8)$$

$$\Delta S^\circ_{1800}\ (3rd) = 84.3\ \text{cal. deg.}^{-1} \quad (9)$$

The errors quoted are the standard deviations for Equations 6 and 8 and the standard deviation of the mean for Equation 7. The (2nd) or (3rd) notation refers to the second law or third law method of calculation.

A C/U ratio of 1.86 in Equation 3 appears to be more accurate (*10*) than the value of 2 used by Piazza and Sinnott. No difference results in the calculated second law heat or entropy. A difference of 1.3 kcal. in the third law heat and of 0.7 cal. deg.$^{-1}$ in the calculated third law entropy results. The assumption of an activity of 0.95 for "UC_2" contributes of the order of 0.2 kcal. to the results quoted in Equation 7. When the auxiliary data are available, the third law treatment is likely to give much more accurate values than those calculated by the second law.

Using the third law data cited above, we compute the heat of formation of $UC_{1.86}$(s), $\Delta H^\circ_{f,298}$, to be −20.5 kcal. per mole. Huber, Head, and Holley (*5*) obtained −21.1 ± 1.4 kcal. per mole by combustion calorimetry.

Agreement within 2.4 kcal. between the second and third law calculations is excellent but is also probably fortuitous. Agreement between the calculated heat of formation of $UC_{1.86}$ with the measurements of Huber, Head, and Holly (*5*) within 0.6 kcal. is also probably somewhat fortuitous. Nevertheless, the agreement is good and comparison between the two denies stabilization of "UC_2" by oxygen, at least to the extent assumed (*7,15*).

Combining the standard deviation reported in Equation 7 with the uncertainty in the heat of formation of UO_2 yields 0.8 kcal. uncertainty in the heat of formation of $UC_{1.86}$. Combination of this result with the uncertainty of Huber, Head, and Holley (*5*) leads to a "best" value of ±0.7 kcal. The "best" value of the heat of formation, ΔH°_{298}, of "UC_2" is thus −20.8 ± 0.7 kcal. per mole.

THE UO_2-"UC_2"-UC-CO SYSTEM

Piazza and Sinnott also studied the experimentally more difficult system UO_2-"UC_2"-UC in equilibrium with CO from 1761° to 1953° K. by measuring the CO partial pressures. The reaction they studied is assumed to be

$$UO_2 + 3.488\ UC_{1.86} = 4.488\ UC + 2CO \quad (10)$$

The thermal data for UC were calculated from the data of Levinson (*11*) and of Harrington and Rowe (*4*) combined with the necessary low temperature data from Westrum *et al.* (*18*). An average ΔC_p of −37.1 cal. °K.$^{-1}$ was calculated over the range 1700° to 2000°K., but for theis calculation we adjusted C_p of UC to 15.53 cal. deg.$^{-1}$ at 2000° K. instead of using the value reported in Table I.

Treating their data in the fashion described above, with a_{UC} and $a_{UC_{1.86}}$ assumed to be 0.95 and a_{UO_2} to be unity, we obtain the equation

$$\Delta F^\circ = 216{,}100 + 37.1\ T \ln T - 380.1\ T\ \text{cal.} \quad (11)$$

The internal consistency of the data is shown by the following:

$$\Delta H^\circ_{298}\ (2nd) = 164.1 \pm 7.5\ \text{kcal.} \quad (12)$$

$$\Delta H^\circ_{298}\ (3rd) = 174.8 \pm 0.3\ \text{kcal.} \quad (13)$$

$$\Delta S^\circ_{1800}\ (2nd) = 64.9 \pm 4.0\ \text{cal. deg}^{-1} \quad (14)$$

$$\Delta S^\circ_{1800}\ (3rd) = 70.6\ \text{cal. deg.}^{-1} \quad (15)$$

The internal consistency is not particularly good; however, this is not unexpected.

Combination of Equations 3 and 10 in an appropriate fashion leads to the reaction

$$UC\ (s) + 0.86\ C\ (\text{graphite}) = UC_{1.86} \quad (16)$$

A ΔH°_{298} of +2.37 kcal., using the third law results, is calculated for Reaction 16. An alternative way of expressing the information is to state that the heat of formation of UC, $\Delta H^\circ_{f,298}$, is computed to be −23.2 kcal. per mole. Huber, Head, and Holley (*6*) have recently remeasured this quantity indirectly by combustion calorimetry in an oxygen bomb and obtained a $\Delta H^\circ_{f,298}$ of −23.3 ± 0.9 kcal. for $UC_{0.996 \pm 0.005}$ and −23.0 ± 1.0 kcal. for $UC_{1.033 \pm 0.005}$.

The agreement of the measurements of Huber, Head, and Holley (*6*) with Piazza and Sinnott (*14*) appears to be exceedingly good. The discrepancy between the second law and third law calculations probably reflects the difficulty of obtaining equilibrium in the system studied by Piazza and Sinnott. It may also reflect a shift in activity of the UC phase with temperature. A "best" value for the heat of formation, $\Delta H^\circ_{f,298}$, of UC can probably be fixed by Huber, Head, and Holley when they have completed their calculations.

Thermodynamic functions calculated from the data cited are tabulated in Table I.

LITERATURE CITED

(1) Conway, J.B., Hein, R.A., *J. Nucl. Mater.* **15**, 149 (1965); private communication.

(2) Dow Chemical Co., Midland, Mich., "JANAF Interim Thermochemical Tables," March 31, 1961.

(3) Farr, J.D., Witteman, W.G., Stone, P.L., Westrum, E.F., Jr., "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," Serge Gratch, ed., p. 162, American Society of Mechanical Engineers, New York, 1965.

(4) Harrington, L.C., Rowe, G.H., "Enthalpy and Heat Capacity of Uranium Monocarbide to 2000° C.," Pratt and Whitney Aircraft, CANEL, **PWAC-426** (1964).

(5) Huber, E.J., Jr., Head, E.L., Holley, C.E., Jr., *J. Phys. Chem.* **67**, 1730 (1963).

(6) Huber, E.J., Jr., private communication.

(7) International Atomic Energy Agency, "The Uranium-Carbon and Plutonium-Carbon Systems," Tech. Rept. Ser. **14**, p. 39 (1963).

(8) Jones, W.M., Gordon, Joseph, Long, E.A., *J. Chem. Phys.* **20**, 695 (1952).

(9) Leitnaker, J.M., "Thermodynamic Properties of Refractory Borides," Los Alamos Scientific Laborabory, Rept. **LA-2402** (1960).

(10) Leitnaker, J.M., Witteman, W.G., *J. Chem. Phys.* **36**, 1445 (1962).

(11) Levinson, L.S., "Carbides in Nuclear Energy," Vol. I, Macmillan, London, 1964.
(12) Levinson, L.S., *J. Chem. Phys.* **38**, 2105 (1963).
(13) Moore, G.E., Kelley, K.K., *J. Am. Chem. Soc.* **69**, 2105 (1947).
(14) Piazza, J.R., Sinnott, M.J., J. CHEM. ENG. DATA **7**, 451 (1962).
(15) Rand, M.H., "Variation of Some Thermodynamic Properties across the UC-UN Solid Solution Range," U.K. Atomic Energy Establishment, Rept. **AERE-M1360**, 2 (1964).
(16) Rand, M.H., Jubaschewski, O., "Thermochemical Properties of Uranium Compounds," Interscience, New York, 1963.
(17) Stull, D.R., Sinke, G.C., *Advan. Chem. Ser.*, No. **18** (1956).
(18) Westrum, E.F., Jr., Seuts, Evan, Lonsdale, H.K., "Advances in Thermophysical Properties at Extreme Temperatures and Pressures," p. 156 American Society of Mechanical Engineers New York, 1965.

RECEIVED for review December 27, 1965. Accepted March 23, 1966. Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

Surface Tension–Viscosity Relation for Liquids

ARNOLD H. PELOFSKY
Department of Chemistry and Directorate of Faculty Research, United States Air Force Academy, Colo.

An empirical equation is proposed, $\gamma = A_{\text{exptl.}}B/\eta$, relating viscosity ($\eta$) to surface tension ($\gamma$) where A and B are dimensional constants. Experimental literature data for 33 liquid systems (organic and inorganic) are used to demonstrate the validity of the equation. Water, benzene, and toluene liquid systems are used to show that the constant B is a function of (Mk/R) where M is the molecular weight, k is the thermal conductivity, and R is the gas constant. The data suggest that this equation may be applicable over the entire liquid phase regime for any given substance.

SEVERAL relations have been postulated relating surface tension of a liquid in air to viscosity. In 1932, Silverman and Roseveare (*9*) postulated that

$$\gamma - {}^{1\!}/_{4} = \frac{A}{\eta} + B \qquad (1)$$

where A and B are empirical constants for a given substance. In 1953, Murkerjee (*5*) postulated that viscosity is related to surface tension by

$$\gamma = \mathrm{K}\eta^{n1/3} \qquad (2)$$

where K and n are empirical constants. In 1956, Sanyal and Mitra (*8*) postulated the following relations:

$$\text{Associated liquids: } T \log \eta - a\gamma^{5/6} = b \qquad (3)$$

$$\text{Nonassociated liquids: } T \log \eta - a\gamma = b \qquad (4)$$

where a and b are empirical constants. In 1962, Pratap and Narsimhan (*7*), suggested that surface tensions and viscosity are related by the following equation:

$$\frac{u_L \cdot \eta \cdot V^{2/3}}{(M \cdot T)^{1/2}} = 9.27_{\text{exptl.}} \; \frac{1.091 \cdot N^{1/3} \cdot \gamma \cdot V_m^{\;2/3}}{R \cdot T} \qquad (5)$$

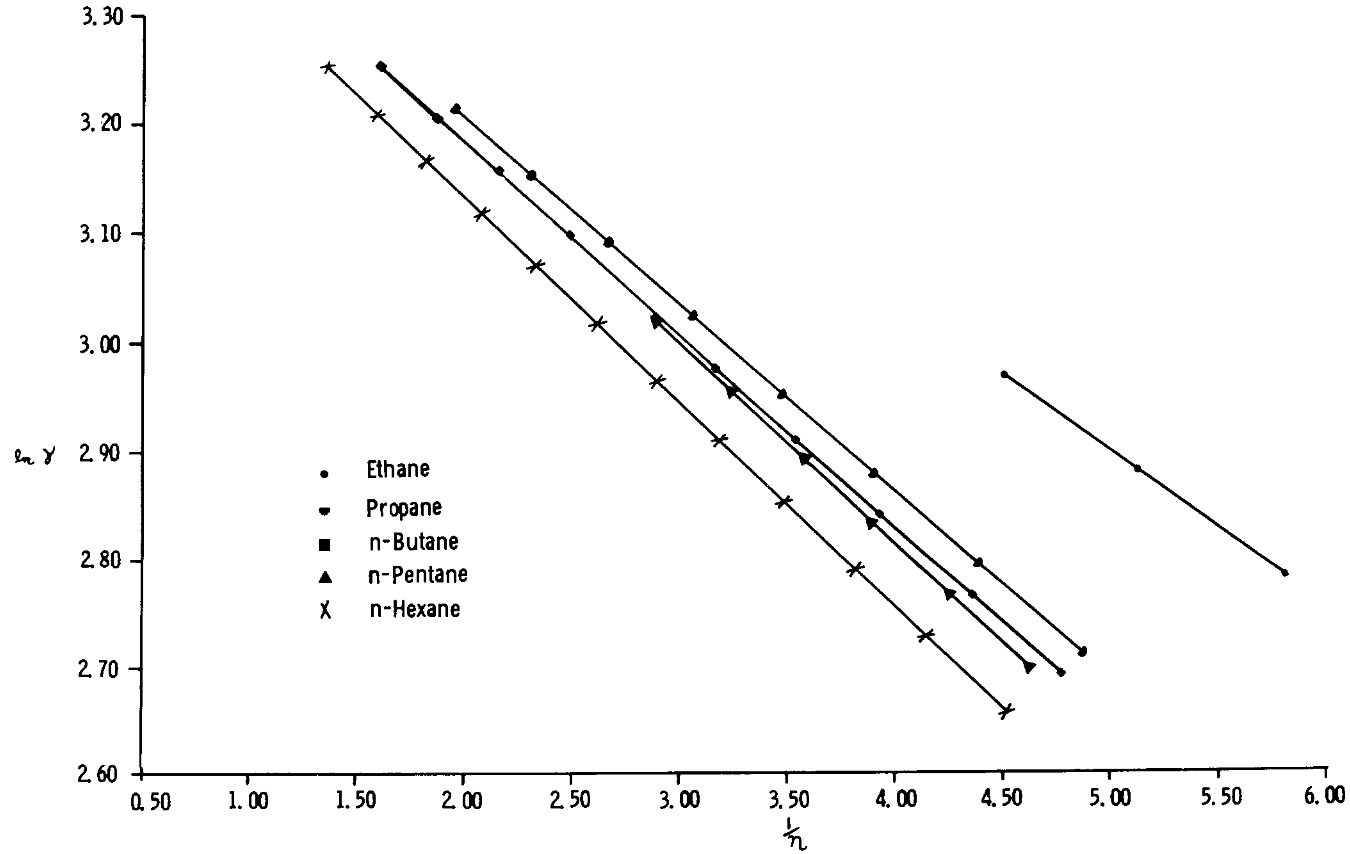

Figure 1. Least squares fit of experimental data for some members of the paraffin series