

## CYCLOHEXANE-DECALIN

The most striking system measured was cyclohexane + decalin (Figure 2). The heats of mixing changed sign at high cyclohexane concentrations. Some measurements were made at 25°C. with decalin having cis-decalin concentrations of 10%, 64%, and 99%. The results were consistent; the heats of mixing changed signs at cyclohexane concentrations of 75, 81, and 88 mole per cent respectively. However, the calorimeter used is not well suited for these measurements. The very small heats of mixing (maximum 42 joules/mole) and the great differences in the vapor pressures of the components make the relative corrections for the vapor space undesirably large.

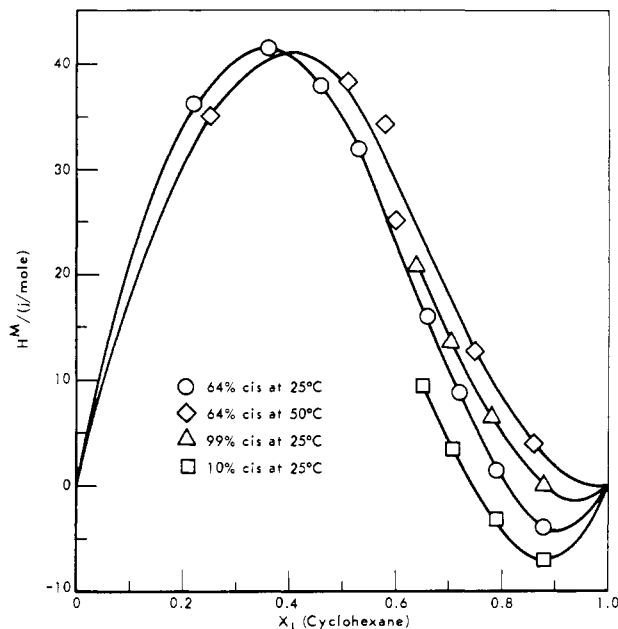


Figure 2. Heats of mixing of cyclohexane + decalin

## ACKNOWLEDGMENT

The author wishes to express his appreciation to W.H. Husing and J.M. Oort, who were largely responsible for the construction of the calorimeter and many of its design features, to R.U. Bonnar for his valuable assistance with the computer programs, and especially to Otto Redlich under whose supervision this work was performed.

## NOMENCLATURE

- $A$  =  $H^M / V\phi_1\phi_2$
- $A_j$  = coefficients in Equation 2
- $B$  =  $H^M / x_1x_2$
- $B_j$  = coefficients in Equation 1
- $H^M$  = excess heat content in j./mole
- $x_i$  = mole fraction of component  $i$
- $V$  = Volume of one mole of the components of the mixture in ml.
- $V_i$  = molar volume of component  $i$  in ml.
- $\phi_i$  = volume fraction of component  $i$

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## Thermodynamic Properties of $\text{Pu}^{239}$ as an Ideal Gas

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THERE IS INSUFFICIENT published information on the plutonium spectrum to permit an accurate calculation of the thermodynamic properties of this element as an ideal monatomic gas. The values presented in this paper can be considered only as estimates because they are based on only the 32 levels listed in Table II. The 9179.05  $\text{cm}^{-1}$  and 10,238.24  $\text{cm}^{-1}$  levels were supplied by Dr. Jean Blaise in a private communication; the others

are from Tableau XXIII of Gerstenkorn (1), the only published values known to the author at the time these calculations were performed.

The highest energy level in Table II is 27,651.22  $\text{cm}^{-1}$ . There are certainly large numbers of higher levels to be expected and there already exists evidence of additional lower levels which have not been published because of some unresolved questions. These factors make it difficult to select an upper temperature at which to terminate the calculations. The paucity of spectroscopic data does

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Table I. Thermodynamic Properties of Pu<sup>239</sup>

Atomic weight = 237.06 gram mole <sup>-1</sup>				
$H_{298.15}^{\circ} - H_0^{\circ} = 1481.75 \text{ cal. mole}^{-1}$				
$S_{298.15}^{\circ} = 42.3196 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$				
Cal. Deg. <sup>-1</sup> Mole <sup>-1</sup>				
T, °K.	$H^{\circ} - H_{298.15}^{\circ}$	C <sub>p</sub>	S <sub>T</sub> - S <sub>298.15}^{\circ}</sub>	$F^{\circ} - H_{298.15}^{\circ}$
	Cal. Mole <sup>-1</sup>			T
298.15	0.00	4.9845	0.0000	42.3196
300.00	9.22	4.9854	0.0308	42.3196
400.00	512.40	5.1037	1.4776	42.5161
500.00	1,035.80	5.3929	2.6443	42.8923
600.00	1,595.71	5.8227	3.6640	43.3240
700.00	2,202.52	6.3185	4.5984	43.7715
800.00	2,859.47	6.8172	5.4749	44.2201
900.00	3,564.80	7.2819	6.3051	44.6638
1000.00	4,314.21	7.6976	7.0943	45.0996
1100.00	5,102.59	8.0618	7.8454	45.5263
1200.00	5,924.98	8.3784	8.5608	45.9429
1300.00	6,776.86	8.6525	9.2425	46.3491
1400.00	7,654.21	8.8887	9.8926	46.7449
1500.00	8,553.44	9.0903	10.5129	47.1302
1600.00	9,471.18	9.2593	11.1052	47.5052
1700.00	10,404.25	9.3969	11.6708	47.8702
1800.00	11,349.54	9.5040	12.2111	48.2253
1900.00	12,304.06	9.5816	12.7271	48.5709
2000.00	13,264.94	9.6313	13.2200	48.9071
2100.00	14,229.46	9.6550	13.6906	49.2342
2200.00	15,195.16	9.6552	14.1398	49.5525
2300.00	16,159.80	9.6345	14.5686	49.8622
2400.00	17,121.47	9.5961	14.9779	50.1635
2500.00	18,078.52	9.5428	15.3686	50.4568
2600.00	19,029.63	9.4777	15.7417	50.7421
2700.00	19,973.76	9.4036	16.0980	51.0198
2800.00	20,910.13	9.3229	16.4385	51.2902
2900.00	21,838.20	9.2379	16.7642	51.5533
3000.00	22,757.64	9.1506	17.0759	51.8096
3100.00	23,668.29	9.0625	17.3745	52.0591
3200.00	24,570.15	8.9749	17.6609	52.3022
3300.00	25,463.32	8.8889	17.9357	52.5391
3400.00	26,348.02	8.8054	18.1998	52.7700
3500.00	27,224.50	8.7248	18.4539	52.9950
3600.00	28,093.10	8.6477	18.6986	53.2145
3700.00	28,954.16	8.5743	18.9345	53.4286
3800.00	29,808.08	8.5046	19.1623	53.6376
3900.00	30,655.22	8.4389	19.3823	53.8416
4000.00	31,495.98	8.3769	19.5952	54.0407
4100.00	32,330.73	8.3187	19.8013	54.2353
4200.00	33,159.84	8.2640	20.0011	54.4255
4300.00	33,983.65	8.2127	20.1949	54.6113
4400.00	34,802.49	8.1646	20.3832	54.7931
4500.00	35,616.66	8.1194	20.5662	54.9709
4600.00	36,426.46	8.0769	20.7442	55.1449
4700.00	37,232.13	8.0370	20.9174	55.3152
4800.00	38,033.93	7.9993	21.0862	55.4820
4900.00	38,832.06	7.9637	21.2508	55.6454
5000.00	39,626.72	7.9299	21.4113	55.8056

not justify going to 5000°K. However, values for the higher temperatures are included to serve the needs of those people who in the absence of available numbers would be compelled to make estimates of their own. For those readers who may be interested in comparing these results with estimates based on other than spectroscopic data, attention is called to the report by Mulford (2), which covers the temperature range 298°K. to 2500°K.

A word about significant figures. The number retained at the higher temperatures is not justified by the accuracy.

Table II. Energy Levels of Pu<sup>239</sup> Used in the Calculations

Level (Cm. <sup>-1</sup> )	J	Level (Cm. <sup>-1</sup> )	J
0.0	0	20,385.4	2
2,203.6	1	20,525.75	1
4,299.6	2	21,227.95	4
6,144.3	3	21,420.95	3
7,774.4	4	23,416.57	2
9,179.05	5	23,766.2	1
10,238.24	6	24,158.75	2
13,517.5	2	24,653.30	1
15,406.8	1	24,751.43	1
15,865.8	1	24,848.73	2
16,734.1	2	25,397.28	1
17,500.88	1	25,617.55	2
17,615.35	2	25,660.90	1
18,346.9	2	25,828.08	4
19,426.2	3	26,633.40	1
		27,536.10	3
		27,651.22	2

However, all the figures printed out by the computer are presented because it is difficult to know or estimate the accuracy when some of the low lying energy levels may be missing in the input data. Furthermore, retaining all the digits will facilitate comparing these numbers with improved results which may become available in the future.

The calculations were performed on an IBM 704 computer using the well known methods of statistical mechanics to be found in many textbooks [for example, Rossini (3), or Mayer and Mayer (4)]. The computer printed out the results reproduced in Table I. The atomic weight of Pu<sup>239</sup> was obtained from Everling and coworkers (5) and all other constants from Cohen, Dumond, Layton, and Rollet (6) with the subsequent revisions of Cohen and Dumond (7). All constants were converted to the chemical scale of atomic weights giving:

$$\text{Gas constant } R = 1.98731 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\alpha = hc/k = 1.43875 \text{ cm. deg.}$$

$$\text{Avogadro's No., } N = 6.02338 \times 10^{23} \text{ molecules mole}^{-1}$$

Also, 1.000272 was used as a conversion factor from chemical to physical scale and 1 cal. = 4.1840 joules.

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