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Standard Data for the Formation of Solid Cobaltous Oxide

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The most recent compilation of thermodynamic properties of cobaltous oxide, in 1970, does not include all of the data now available. We have, therefore, made a new critical evaluation and a new treatment of all data, which lead to the best value for the standard enthalpy of formation of solid cobaltous oxide: $\Delta H_f°(\text{CoO, s, 298.15 K}) = -237500 \pm 400$ J mol^{-1}.

I. Introduction

The thermodynamic properties of stoichiometric defects in solid cobaltous oxide have been determined by measuring the electronic conductivity as a function of composition, this latter being imposed by contact with a cobalt-platinum electrode (*44*). In addition to other data, the exploitation of the results requires standard thermodynamic data for the formation of solid cobaltous oxide.

The most recent critical evaluation, that of JANAF (*1*), dates from December 1970 and does not include all of the data now available, for instance, those after 1969 (*11*, *18-21*, *27-30*, *46*). We have therefore made a new critical review of these properties, the results of which we present here.

II. Previous Studies

Direct determination of the standard heat of formation of cobaltous oxide by combustion calorimetry gives the following results:

$$\Delta H_f°(298.15\text{ K}) = -240400\text{ J mol}^{-1}\ (31)$$
$$-240600 \pm 800\text{ J mol}^{-1}\ (32)$$
$$-238700 \pm 1200\text{ J mol}^{-1}\ (33)$$

Table I summarizes results of experiments on cobaltous oxide, obtained from equilibria of reduction by hydrogen (*2-11*), carbon monoxide (*12-20*), and methane (*21*), as well as a direct investigation by mass spectrometry of the CoO-Co-O_2 equilibria (*22*).

Table II summarizes results of experiments on cobaltous oxide determined from emf measurements with a solid electrolyte cell and various reference electrodes (*23-30*, *46*).

Results published in terms of cal mol^{-1} have been converted into J mol^{-1} on the basis of 1 cal = 4.1840 J.

Finally it should be noted that compilations (*34*, *35*) prior to JANAF (*1*) will not be taken into account here, as they were made before the standard entropy $S°(298.15\text{ K})$ of cobaltous oxide was available, this only being measured 3 yr later (*37*) in 1957.

III. Calculations from the Second and Third Laws

The thermodynamic properties have been calculated by the methods of the second and third laws (*37*).

Using measured values of the ratios H_2O/H_2 and CO_2/CO and the electromotive force values, we have calculated the standard free energy of formation $\Delta G_f°(T)$ of cobaltous oxide with standard formation data of H_2O, CO_2, CO, $Fe_{0.947}O$, and Cu_2O taken from JANAF (*37*) and of NiO taken from Kellog (*38*).

The second-law calculations have been made with the enthalpy and entropy increments of oxygen (*37*), cobalt (*37*), and cobaltous oxide (*1*). Thus for each set of measurements by the various workers, we have calculated the standard enthalpy of formation $\Delta H_f°(298.15\text{ K})$ and the standard entropy of formation $\Delta S_f°(298.15\text{ K})$ of cobaltous oxide. These results are listed in columns 5 and 6 of Tables I and II.

For the calculations using the method of the third law, we have used the value $\Delta S_f°(298.15\text{ K}) = -79.54 \pm 0.77$ J mol^{-1} K^{-1} for the standard entropy of formation of cobaltous oxide calculated from the standard entropies at 298.15 K given by the JANAF tables for oxygen and cobalt (*37*) and for cobaltous oxide (*1*). Results only published in the form of a linear regression (*21*, *24*, *27-29*, *46*) have been treated by the third law with the midpoint of the measuring range. The values of $\Delta H_f°(298.15\text{ K})$ obtained by this method are given in column 7 of Tables I and II.

IV. Discussion and Results

Examination of the three calorimetric determinations of the standard heat of formation of cobaltous oxide leads us to eliminate the two prior determinations, in 1910 (*31*) and in 1937 (*32*), because these too negative values can be explained by the lack of the useful corrections mentioned by the third author (*33*) (overoxidation and silicate formation). We can only use the value of −238 700 ± 1200 J mol^{-1} of ref *33*.

Examination of the second- and third-law results for each group of measurements leads us to make a selection. Firstly we have eliminated measurements (*2*, *3*, *6*, *10*, *15*, *22*, *24*, *46*) which lead to a second-law standard entropy of formation $\Delta S_f°(298.15\text{ K})$ which is more than 4 J mol^{-1} K^{-1} greater or less than the value −79.54 J mol^{-1} K^{-1} obtained by direct calorimetry. Secondly we have eliminated the measurements (*4*, *8*, *21*) which lead to a third-law standard enthalpy of formation $\Delta H_f°(298.15\text{ K})$ either abnormally high or low ($>-236\,000$ or $<-239\,000$ J mol^{-1}) and which must include too great a systematic error.

Finally for an overall second-law calculation, we cannot use the results (*21*, *24*, *27-29*) which are only published in the form of a linear regression, as our calculation is only valid if the basic experimental results are used. In this way, we have selected 109 measurements by 16 different sets of workers (*5*, *7*, *9*, *11-14*, *16-20*, *23*, *25*, *26*, *30*) for a new second-law calculation which gives the following results (statistical uncertainties are given at 95% confidence limits (*45*)):

$$\Delta H_f°(298.15\text{ K}) = -237541 \pm 368\text{ J mol}^{-1}$$

$$\Delta S_f°(298.15\text{ K}) = -79.65 \pm 0.27\text{ J mol}^{-1}\text{ K}^{-1}$$

For the third-law calculation, we have not eliminated the four sets of results (*27-29*) which are published in the form of linear regressions; the mean value of overall results of these 113 measurements from 20 different sets of workers is

$$\Delta H_f°(298.15\text{ K}) = -237368 \pm 96\text{ J mol}^{-1}$$

$$\Delta S_f°(298.15\text{ K}) = -79.54\text{ J mol}^{-1}\text{ K}^{-1}$$

The uncertainty of $\Delta H_f°(298.15\text{ K})$ is given at the statistical 95% confidence limit (*45*) from the distribution of the 113 experimental values without taking into account the JANAF uncertainty of $\Delta S_f°(298.15\text{ K})$ which is 0.77 J mol^{-1} K^{-1}. If we

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Table I. Thermodynamic Properties of Cobaltous Oxide from Equilibrium Measurements

ref	e[a]	temp range, K	n[b]	$\Delta H_f°$(298.15 K), 2nd law, J mol^{-1}	$\Delta S_f°$(298.15 K), 2nd law, J mol^{-1} K^{-1}	$\Delta H_f°$(298.15 K), 3rd law, J mol^{-1}
2	H	1073-1323	3	−226 670	−70.81	−237.348
3	H	723-1023	2	−255 625	−91.66	−245 044
4	H	1523	1			−233 994
5	H	608-843	4	−240 121	−83.13	−237 460
6	H	695-1194	6	−242 557	−85.48	−236 940
7	H	739-898	4	−237 947	−79.44	−238 030
8	H	1273	1			−232 882
9	H	1073-1498	5	−241 424	−82.60	−237 483
10	H	773-1173	5	−232 600	−73.64	−238 339
11	H	606-1250	13	−237 265	−79.67	−237 147
12	C	1173	1			−237 999
13	C	723-843	3	−237 184	−78.83	−237 736
14	C	836-1134	7	−234 813	−76.74	−237 564
15	C	996-1396	5	−248 087	−84.83	−241 739
16	C	1273-1673	3	−237 719	−78.88	−238 692
17	C	1473-1673	3	−234 059	−77.09	−237 903
18	C	1323	1			−237 279
19	C	1373-1573	2	−236 974	−78.96	−237 822
20	C	1423	1			−237 000
21	M	1073-1423	(n)	−237 350	−77.78	−239 545
22	O	1578-1744	20	−196 600	−60.67	−229 430

[a] e = nature of equilibrium studied: reduction of CoO by H_2 (H), CO (C), CH_4 (M), or mass-spectrographic study of Co, CoO, O_2 (O).
[b] n = number of experimental points: symbol (n) means an analytical equation (linear regression) without specifying the value of n.

Table II. Thermodynamic Properties of Cobaltous Oxide from Emf Measurements

ref	r[a]	temp range, K	n[b]	$\Delta H_f°$(298.15 K), 2nd law, J mol^{-1}	$\Delta S_f°$(298.15 K), 2nd law, J mol^{-1} K^{-1}	$\Delta H_f°$(298.15 K), 3rd law, J mol^{-1}
23	Fe	1173-1373	5	−240 840	−81.67	−238 121
24	air	996-1496	(n)	−245 718	−87.70	−236 148
25	air	1073-1273	8	−239 340	−81.90	−236 544
26	air	1473	1			−237 538
27	Cu	853-1253	(14)	−237 756	−80.79	−236 325
27	Ni	853-1253	(16)	−237 739	−80.92	−236 310
28	air	973-1773	(72)	−237 192	−79.96	−236 628
29	air	1073-1673	(n)	−235 099	−78.06	−237 128
30	air	1473-1722	32	−234 698	−77.88	−237 345
30	air	1742-1833	16	−238 955	−80.56	−237 139
46	Ni	1173-1352	(n)	−241 697	−83.14	−237 141
46	Fe	1129-1301	(n)	−251 514	−90.18	−238 627
46	Cu	980-1140	(n)	−220 741	−63.98	−237 240
46	air	963-1113	(n)	−250 955	−91.01	−239 051

[a] r = nature of the reference electrode of the galvanic cell: Fe-FeO (Fe); Cu-Cu_2O (Cu); Ni-NiO (Ni); O_2 in air (air). [b] n = number of experimental points; a figure in parentheses indicates the number of points used to establish the analytical equation (linear regression) published instead of the original experimental values; symbol (n) means that n is unknown.

account for this last uncertainty, we obtain a supplementary uncertainty of 1000 J mol^{-1} for $\Delta H_f°$(298.15 K).

The third-law final value for $\Delta H_f°$(298.15 K) is −237 368 ± 1000 J mol^{-1}.

It can be seen that there is excellent agreement between the calorimetric result (*33*) and the results for the second and third laws when applied to more than 109 measurements made by 20 sets of workers with different techniques.

However, the second law leads to more precise results than the third law, and we can obtain only a rounded final value with the second-law result:

$$\Delta H_f°(\text{CoO, 298.15 K}) = -237500 \pm 400 \text{ J mol}^{-1}$$

$$\Delta S_f°(\text{CoO, 298.15 K}) = -79.6 \pm 0.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note that Rau and Guedes de Carvalho (*11*) applied a third-law treatment to their own measurements of the CoO + H_2 = Co + H_2O equilibrium using the standard specific heats determined by Armstrong and Grayson-Smith (*41*) instead of the values compiled in the JANAF tables (*37*). Taking into account the uncertainty in their experiments, they found

$$\Delta H_f°(298.15 \text{ K}) = -237500 \pm 1500 \text{ J mol}^{-1}$$

Budgen and Pratt (*27*) also used a third-law treatment with their measurements using the enthalpy and entropy data published by Kelley (*40*) and Kubaschewsky et al. (*42*). They give

$$\Delta H_f°(298.15 \text{ K}) = -236800 \pm 130 \text{ J mol}^{-1}$$

However, their result depends on the values used for the standard free energies of the reference equilibrium Ni-NiO and Cu-Cu_2O and cannot therefore be directly compared with the values given above.

We can note however that emf studies (all but three) suggest an entropy larger than the JANAF value used for the third law. This could perhaps be explained by a fallacious lowering of emf with increasing temperature.

Note also that the more recent direct determination of the standard heat of formation of cobaltous oxide by combustion calorimetry, in 1954 (*33*), is quite consistent with our result, unlike the two earlier determinations (*31*, *32*) mentioned in section II of this study.

Note also that the most recent (1969) NBS bulletin (*43*) gives the value

$$\Delta H_f°(298.15 \text{ K}) = -237900 \text{ J mol}^{-1}$$

and the 1974 JANAF compilation (*1*), with the CoO table established December 31, 1970, leads to

$$\Delta H_f°(298.15\ \mathrm{K}) = -237700 \pm 420\ \mathrm{J\ mol^{-1}}$$

However, we can note that these two tables do not include the same recent data after 1969.

Conclusion

The values which we have selected do not disagree with any other measurements, and we may conclude that the best value for the standard enthalpy of formation of solid cobaltous oxide is

$$\Delta H_f°(\mathrm{CoO,\ s,\ 298.15\ K}) = -237500 \pm 400\ \mathrm{J\ mol^{-1}}$$

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Solubility of Hydrogen in 9-Methylanthracene, Dibenzofuran, and 2-Ethylanthraquinone at High Temperatures and Pressures

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Solubility of hydrogen was measured in 9-methylanthracene and dibenzofuran at 100, 150, 200, and 250 °C and for pressures up to ca. 258 atm. For ethylanthraquinone (mp ca. 110 °C), the solubility was measured at 125, 150, and 200 °C and up to ca. 250 atm. The solubility data were used to calculate Henry's constants of hydrogen in the three aromatic compounds.

Introduction

Solubility data are needed for efficient design of pressure blow down vessels in a chemical process. In coal liquefaction processes, the hydrogenation reactor is followed by a high-pressure and then a low-pressure separator. Hydrogen solubility data in polyaromatic hydrocarbons is of particular interest in the designing of these separators. This work was initiated to measure the effect of structure on the solubility of hydrogen in three-ring aromatic compounds, one of the major constituents of coal liquefaction products.

Experimental Section

The apparatus that was used to measure the solubility of hydrogen in the three polyaromatic compounds was described in an earlier publication (*2*). The only change was the replacement of a thermocouple with a calibrated platinum resistance thermometer for the measurement of liquid bath temperatures.

All three polyaromatic compounds were purchased from Aldrich Chemical Co. These were further purified to at least 99.9% purity by zone purification technique. Hydrogen, with a purity of 99.995%, was purchased from Matheson Gas Co.

Results and Discussion

The solubility data for hydrogen in 9-methylanthracene, 2-ethylanthraquinone, and dibenzofuran are tabulated in Tables I-III. Figure 1 shows hydrogen solubility as a function of temperature and pressure for all of the compounds. 2-Ethylanthraquinone was found to be unstable above 200 °C. Since it showed significant hydrogenation at 250 °C, solubility mea-

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