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《**Original**》

Atom Number Densities for Uranyl Nitrate Solution

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질산우라늄용액의 구성원소별 원자수밀도

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Abstract

An empirical formula for determining water content as functions of uranium concentration and nitric acid normalities in uranyl nitrate solutions has been derived from a least-squares analysis of experimental data, i.e., uranium concentration, nitric acid normalities and solution densities for a large number of $UO_2(NO_3)_2$ solutions. The formula derived is $Q=1-0.3628C-0.0327H^+$ where Q,C, and H^+ stand for water content (g/cc), uranium concentration (g/cc), and nitric acid normality, respectively. Atom number densities and nuclear criticality for hypothetical uranyl nitrate solutions have been calculated by using the empirical formula, and compared with the results obtained on the basis of uranium concentration, nitric acid normality, and solution density.

The empirical formula derived in this study seems to be useful in uranium concentrations ranging from 0.295g/cc down to 0.004g/cc and nitric acid normality from 5.06 to 1.00.

요 약

여러가지 질산우라늄용액에 대한 우라늄의 용존농도, 질산의 노르말농도 및 용액의 밀도등을 측정하여 얻은 결과를 최소자승법으로 분석한 후 우라늄의 용존농도와 질산의 노르말농도만을 알므로서 질산우라늄용액속에 들어있는 물의 함량을 결정할 수 있는 실험식, $Q=1-0.3628C-0.0327H^+$,을 유도하였다. 여기서 Q, C 및 H^+는 각각 물함량(g/cc), 우라늄의 용존농도(g/cc) 및 질산의 노르말농도를 뜻한다. 그리고 이 유도식을 써서 임의 우라늄용액에 대한 구성원소별 원자수밀도와 핵임계도를 산출하고 그 결과를 우라늄의 용존농도, 질산의 노르말농도 및 용액의 밀도를 근거로 하여 얻은 값과 비교해 보았다.

그 결과 유도식은 우라늄의 용존농도 0.004~0.295g/cc 및 질산의 노르말농도 1.00~5.06 사이에서 유용하게 쓰일 수 있을 것으로 보였다.

1. Introduction

A prior knowledge of the water content in a certain nitrate solution of fissile materials is required to determine atom number densities therein. In general, a determination of the water content is based on the experimental data such as fissile material concentrations, nitric acid normality, and solution densities, which make it necessary to perform tedious laboratory measurements.[1]

Comparatively a simple method has been suggested for that. For example, an empirical formula had been presented for determining the water content as functions of plutonium concentration and nitric acid normality in a certain plutonium nitrate solution,[2] and was later corrected[3] by Richey. Dikinson[4] had examined the Richey's formula to find out its validity.

Unfortunately no empirical formula has been known for uranyl nitrate solutions. Therefore, this work has been carried out to propose an empirical formula for them. This is to derive it from a least-squares analysis of the experimental data for a large number of uranyl nitrate solutions. Consequently atom number densities on the basis of the derived formula have been calculated and compared with those for actual solutions, and effect of differences in atom number densities on nuclear criticality tested.

2. Water Content and Atom Number Density

If it is assumed that the solution is composed of uranyl nitrate as $UO_2(NO_3)_2$, nitric acid (HNO_3), and water (H_2O), the water content, Q(g/cc), can be determined from the formula:

$$Q=\rho-\left\{C+\frac{62.0064}{0.6023}N(NO_3^-)+\frac{15.9999}{0.6023}N(O)+0.0630H^+\right\} \cdots\cdots (1a)$$

or

$$=\rho-\left\{C+\frac{78.0063}{0.6023}N(NO_3^-)+0.0630H^+\right\} \cdots\cdots (1b)$$

where

ρ: the solution density in grams per cubic centimeter (g/cc)

C: the uranium concentration in grams per cubic centimeter (g/cc)

$N(NO_3^-)$: the number density for nitrate ions from $UO_2(NO_3)_2$ (nitrate ions per barn-cm)

N(O): the number density for oxygen (oxgen numbers per barn-cm)

H^+: the nitric acid normality (n HNO_3). Because the acidity under consideration in this study is larger than 1.00n, the hydrolysis of UO_2^{2+} may be small enough to be neglected.[6),7]

The numerical factors of 62.0064, 15.9999, and 78.0063 in Eqs. (1a) and (1b) stand for weight of nitrate ions, atomic weight of oxygen, and weight of nitrate ions plus atomic weight of oxygen, respectively. The numerical factor of 0.6023 represents Avogadro's number multiplied by barn/cm^2 ($=10^{-24}$) while the factor of 0.0630 means one thousandth of molecular weight for nitric acid.

The normalized formula for calculating the water content may be

$$Q=1-AC-BH^+ \cdots\cdots (1c)$$

Here A and B are parameters to be determined from experiments. In fact, this work is to find out A and B experimentally.

The number density for water molecules (molecules per barn-cm), $N(H_2O)$, is correspondingly given by

$$N(H_2O)=0.0334\left[\rho-\left\{C+\frac{78.0063}{0.6023}N(NO_3^-)+0.0630H^+\right\}\right] \cdots\cdots (2a)$$

or

$$=0.0334(1-AC-BH^+) \cdots\cdots (2b)$$

The subsequent atom number densities for a certain uranyl nitrate solution is obtained by

$$N(^{253}U)=\frac{fC(0.6023)}{235.0439} \cdots\cdots (3a)$$

$$N(^{238}U)=\frac{(1-f)C(0.6023)}{238.0508} \cdots\cdots (3b)$$

$$N(H)=2N(H_2O)+N(HNO_3) \cdots\cdots (3c)$$

$$N(N)=N(HNO_3)+N(NO_3^-) \cdots\cdots (3d)$$

$$N(O)=N(H_2O)+3N(HNO_3)+3N(NO_3^-)+2N(UO_2)=N(H_2O)+3N(HNO_3)+4N(NO_3^-) \cdots\cdots (3e)$$

$$N(UO_2)=N(^{235}UO_2)+N(^{238}UO_2)=N(^{235}U)+N(^{238}U)=\frac{1}{2}N(NO_3^-) \cdots\cdots (3f)$$

$$N(NO_3^-)=2\{N(^{235}U)+N(^{238}U)\} \cdots\cdots (3g)$$

$$N(HNO_3)=0.0006023H^+ \cdots\cdots (3h)$$

in which $N(^{235}U)$, $N(^{238}U)$, $N(H)$, $N(N)$, $N(UO_2)$, and $N(HNO_3)$ stand for the number density (in terms of nuclei or molecules per barn-cm) of quantity in parentheses, respectively.

3. Experimental

A variety of uranyl nitrate solutions were prepared and a subsequent measurements of uranium concentrations, nitric acid normalities, and solution densities performed. In this study, the HNO_3 reagent from Merck Co. was used while uranium sample in the form of $UO_2(NO_3)_2$ $6H_2O$ was from Fischer Co. In order to reduce possible impurities, the distilled water employed here was repurified, by using an ion-exchange resin. The resulting conductivity of the purified water was less than 1×10^{-6} ohm^{-1} cm^{-1}.

Uranium isotopic composition has been measured by means of a mass spectrometer (CAMECA, Model TSN-206 SA) and the results are summarized in Table 1. For convenience' sake, the even number isotopic elements are lumped into ^{238}U in this work. A measurement of nitric acid normalities was made by using the conventional pH-titration method. Apparent concentration of uranium was obtained with

Table 1. Isotopic Composition of Uranium under Consideration

Isotope	Ratio	wt %
^{234}U	0.000016	0.0015
^{235}U	0.002396	0.2360
^{236}U	0.000054	0.0053
^{238}U	1.000000	99.7572

oxidation-reduction titrimetry[5], and the true value determined by comparing with a standard uranium metal of NBS-960. The solution densities were measured by employing a pycnometer. A series of the experiments were done under the constant temperature of 26.0 ± 0.1°C.

4. Results and Discussion

In Table 2, presented is the water content obtained by Eq. (2) with experimental data on multiple samples, giving uranium concentrations, nitric acid normalities, and solution densities. Fig. 1 illustrates the water content as a function of uranium concentrations with varying nitric acid normalities. The solid lines as can be seen in Fig. 1 represent the least-squares fits through the experimental data. In general, the slopes appear to be decreasing with nitric acid normalities. Such a phenomenon may stem from the hydrolysis of uranium dissolved. In aqueous uranyl solution, there exist chemical species of uranium such as UO_2^{2+} and $UO_2(OH)^+$.[6),7)] In strong acid solution free uranyl ion (UO_2^{2+}) is dominant over the hydrolyzed species while $UO_2(OH)^+$ due to hydrolysis reaction [$UO_2^{2+}+H_2O\rightleftarrows UO_2(OH)^++H^+$] is comparatively high in dilute acid solution. According to Allard et al.,[7)] there may be chemical species of uranium, e.g., $UO_2(OH)^+$ and $(UO_2)_2(OH)_2^{2+}$, in nitric acid normalities lower than 0.1n. Therefore, an increment of $UO_2(OH)^+$ content results naturally in a decrement of water content.

Table 2. Water Content in Various Uranyl Nitrate Solutions

HNO_3 Normality, H^+	Uranium Conc., C(g/cc)	Solution Density, ρ(g/cc)	Water Content, Q(g/cc)	HNO_3 Normality, H^+	Uranium Conc., C(g/cc)	Solution Density, ρ(g/cc)	Water Content, Q(g/cc)
1.00	4.410E-3	1.035	9.64687E-1	3.16	1.031E-1	1.231	8.61262E-1
1.00	7.360E-3	1.038	9.62804E-1	3.16	1.472E-1	1.287	8.44161E-1
1.00	1.472E-2	1.048	9.60620E-1	3.16	2.208E-1	1.383	8.18310E-1
1.00	2.945E-2	1.067	9.55237E-1	3.16	2.945E-1	1.482	7.95460E-1
1.00	4.417E-2	1.086	9.49870E-1	3.79	4.150E-3	1.122	8.76311E-1
1.00	7.361E-2	1.126	9.41136E-1	3.79	1.037E-2	1.130	8.74015E-1
1.00	1.472E-1	1.222	9.15269E-1	3.79	1.659E-2	1.139	8.72718E-1
1.00	2.208E-1	1.319	8.90418E-1	3.79	2.074E-2	1.145	8.71849E-1
1.00	2.945E-1	1.413	8.62568E-1	3.79	4.148E-2	1.168	8.60517E-1
1.90	4.150E-3	1.063	9.36406E-1	3.79	1.037E-1	1.250	8.39520E-1
1.90	1.037E-2	1.070	9.33109E-1	3.79	1.452E-1	1.304	8.24823E-1
1.90	1.659E-2	1.079	9.31813E-1	3.79	2.281E-1	1.411	7.94594E-1
1.90	2.074E-2	1.084	9.29943E-1	3.79	2.904E-1	1.488	7.68466E-1
1.90	4.148E-2	1.111	9.22611E-1	5.06	4.150E-3	1.162	8.36284E-1
1.90	1.037E-1	1.193	9.01615E-1	5.06	7.360E-3	1.165	8.33971E-1
1.90	1.452E-1	1.248	8.87918E-1	5.06	1.472E-2	1.177	8.33787E-1
1.90	2.281E-1	1.356	8.58689E-1	5.06	2.208E-2	1.185	8.29604E-1
1.90	2.904E-1	1.436	8.35560E-1	5.06	4.417E-2	1.215	8.23037E-1
3.16	4.410E-3	1.104	8.97579E-1	5.06	1.037E-1	1.288	7.97494E-1
3.16	7.360E-3	1.107	8.95696E-1	5.06	1.472E-1	1.343	7.80436E-1
3.16	1.472E-2	1.116	8.92512E-1	5.06	2.208E-1	1.435	7.50586E-1
3.16	2.208E-2	1.126	8.90329E-1	5.06	2.503E-1	1.475	7.41769E-1
3.16	4.417E-2	1.155	8.82762E-1				

Note: 1. E-3 should be read by $\times 10^{-3}$.
2. Experimental errors in H^+, C, and ρ are given by $<\pm 0.1\%$, $<\pm 0.5\%$, and $<\pm 0.05\%$, respectively.

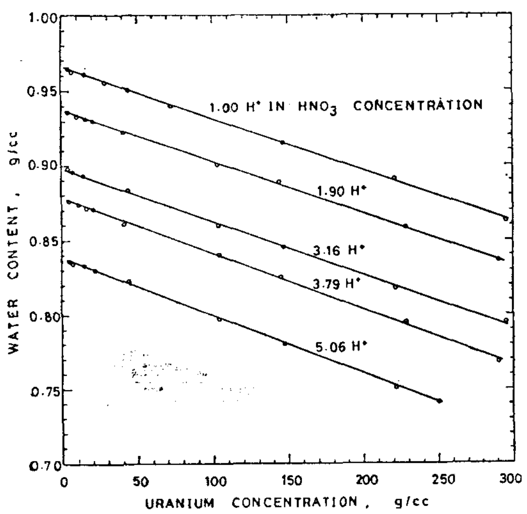

Fig. 1. Relationship of Uranium Concentrations vs. Water Content in Uranyl Nitrate Solution

From the least-squares analysis the parameters A and B in Eq. (1c) were determined to be 0.3628 and 0.0327, respectively, leading to a formula for the water content as functions of uranium concentions and nitric acid normalities only:

$$Q = 1 - 0.3628C - 0.0327H^+ \quad \cdots\cdots (4)$$

This formula [Eq. (4)] finds an application for uranium concentrations ranging from 0.29454 g/cc down to 0.00415g/cc and nitric acid normality from 5.06 to 1.00.

The hydrogen and oxygen number densities calculated on the basis of the derived formula [Eq. (4)] are compared with those of Eq.(1b), and the results are given in Table 3. As is shown in Table 3, the hydrogen number densities from Eq.(4) overestimated actual densities

Table 3. Comparison of Atom Number Densities Based on Eqs. (1b) and (4) for Uranyl Nitrate Solutions

Solution Density, ρ(g/cc)	Uranium Conc., C(g/cc)	^{235}U Fraction, f	HNO_3 Normality, H^+	Hydrogen Number Density (atoms/barn-cm)			Oxygen Number Density (atoms/barn-cm)		
				Based on Eq. (1b)	Based on Eq. (4)	Percent Difference	Based on Eq. (1b)	Based on Eq. (4)	Percent Difference
1.035	0.00441	0.00236	1.00	0.064991	0.065060	0.110	0.034091	0.034125	0.10
1.038	0.00736	"	"	0.065866	0.064988	0.190	0.034088	0.034149	0.18
1.048	0.01472	"	"	0.064720	0.064810	0.140	0.034164	0.034209	0.13
1.067	0.02945	"	"	0.064361	0.064453	0.140	0.034282	0.034329	0.14
1.086	0.04417	"	"	0.064002	0.064097	0.150	0.034401	0.034448	0.14
1.126	0.07361	"	"	0.064319	0.063419	−0.061	0.034705	0.034688	−0.05
1.222	0.14723	"	"	0.061693	0.061601	−0.150	0.035332	0.035286	−0.13
1.319	0.22084	"	"	0.060034	0.059818	−0.360	0.035993	0.035885	−0.30
1.413	0.29445	"	"	0.058175	0.058036	−0.240	0.036554	0.036484	−0.19
1.063	0.00415	"	1.90	0.063646	0.063645	−0.002	0.034768	0.034767	0.00
1.070	0.01037	"	"	0.063426	0.063494	0.110	0.034784	0.034818	0.10
1.079	0.01650	"	"	0.063339	0.063343	0.010	0.034866	0.034868	0.01
1.084	0.02074	"	"	0.063214	0.063243	0.040	0.034888	0.034902	0.04
1.111	0.04148	"	"	0.062725	0.062741	0.020	0.035063	0.035071	0.02
1.193	0.10370	"	"	0.061324	0.061234	−0.150	0.035622	0.035577	−0.13
1.248	0.14520	"	"	0.060409	0.060229	−0.300	0.036005	0.035914	−0.25
1.356	0.22810	"	"	0.058458	0.058221	−0.410	0.036707	0.036589	−0.32
1.436	0.29040	"	"	0.050692	0.056712	−0.360	0.037196	0.037095	−0.27
1.104	0.00441	"	3.16	0.061813	0.061648	−0.270	0.035754	0.035672	−0.23
1.107	0.00736	"	"	0.061687	0.061577	−0.180	0.035751	0.035696	−0.15
1.116	0.01472	"	"	0.061475	0.061399	−0.120	0.035794	0.035755	−0.11
1.126	0.02208	"	"	0.061329	0.061220	−0.180	0.035870	0.035815	−0.15
1.155	0.04417	"	"	0.060824	0.060685	−0.230	0.036064	0.035995	−0.19
1.231	0.10397	"	"	0.059290	0.059237	−0.090	0.036508	0.036481	−0.07
1.282	0.14723	"	"	0.058238	0.058189	−0.100	0.036862	0.036833	−0.08
1.383	0.22084	"	"	0.056522	0.056409	−0.200	0.037489	0.037432	−0.15
1.482	0.29454	"	"	0.054987	0.054622	−0.660	0.038214	0.038031	−0.48
1.122	0.00415	"	3.79	0.060773	0.060659	−0.190	0.036177	0.036121	−0.16
1.130	0.01037	"	"	0.060620	0.060509	−0.180	0.036227	0.036171	−0.15
1.129	0.01659	"	"	0.060633	0.060358	−0.290	0.036309	0.036222	−0.24
1.145	0.02074	"	"	0.060475	0.060258	−0.360	0.036364	0.036255	−0.30
1.168	0.04148	"	"	0.059719	0.059755	0.060	0.036406	0.036424	0.05
1.250	0.10370	"	"	0.058317	0.058249	−0.120	0.036965	0.036930	−0.09
1.304	0.14520	"	"	0.057336	0.057244	−0.160	0.037314	0.037268	−0.12
1.411	0.22810	"	"	0.055319	0.055236	−0.150	0.037982	0.037942	−0.11
1.488	0.29040	"	"	0.053575	0.053727	0.280	0.038372	0.038449	0.20
1.162	0.00415	"	5.06	0.058866	0.058654	−0.360	0.037136	0.037030	−0.29
1.165	0.00736	"	"	0.058712	0.058576	−0.230	0.037124	0.037056	−0.18
1.177	0.01472	"	"	0.058700	0.058398	−0.510	0.037267	0.007116	−0.41
1.185	0.02208	"	"	0.058420	0.058219	−0.340	0.037276	0.037176	−0.27
1.215	0.04417	"	"	0.057982	0.057684	−0.510	0.037504	0.037355	−0.40
1.288	0.10370	"	"	0.056277	0.056243	−0.060	0.037857	0.037840	−0.05
1.343	0.14723	"	"	0.055139	0.055188	0.090	0.038169	0.038194	0.07
1.435	0.22084	"	"	0.053146	0.053406	0.490	0.038552	0.038792	0.34
1.475	0.25033	"	"	0.052558	0.052692	0.250	0.038965	0.039032	0.17

Table 4. Characteristics of Some Hypothetical Uranyl Nitrate Soution

Case	Solution Density, ρ(g/cc)	Uranium Conc., C(g/cc)	^{235}U Fraction, f	HNO_3 Normality, H^+	Hydrogen Number Density (atoms/b−cm)			Oxygen Number Density (atoms/b−cm)		
					Based on Eq. (1b)	Based on Eq. (4)	Percent Difference	Based on Eq. (1b)	Based on Eq. (4)	Percent Difference
1	1.086	0.04417	93.5	1.00	6.39793E-2	6.40969E-2	0.18	3.44001E-2	3.44589E-2	0.17
2	1.356	0.22810	93.5	1.90	5.83394E-2	5.82210E-2	−0.12	3.67028E-2	3.66436E-2	−0.16
3	1.155	0.04417	93.5	3.16	6.08010E-2	6.06853E-2	−0.19	3.60634E-2	3.60055E-2	−0.16
4	1.488	0.29040	93.5	3.79	5.34232E-2	5.37271E-2	0.57	3.83667E-2	3.85667E-2	0.40
5	1.435	0.22084	93.5	5.06	5.30310E-2	5.34058E-2	0.71	3.86581E-2	3.88455E-2	0.48

Note: E-2 should be read by $\times 10^{-2}$.

Table 5. Critical Radii of Bare Sphere Uranyl Nitrate Solution

Case	Percent Difference in N(H)	Critical Radius (cm) for Bare Sphere		Percent Difference in Critical Radii
		Based on Eq. (1b)	Based on Eq. (4)	
1	0.18	21.1134	21.0885	−0.12
2	−0.20	16.7286	16.7592	0.18
3	−0.19	22.1456	22.1724	0.12
4	0.57	17.4802(17.5410)*	17.3921(17.6700)*	−0.50
5	0.71	17.8687	17.7596	−0.61

* Values in parenthesis were obtained by means of Monte Carlo computer code, KENO-IV.

[from Eq.(1b)] ranging from an underestimation of 0.66% to an overestimation of 0.49% and averaging out to an overestimation of 0.084%. Meanwhile, the discrepancy between Eqs.(1b) and (4) for the oxygen number densities was scattered ranging from an underestimation of 0.48% to an overestimation of 0.44% and averaging out to an overestimation of 0.059%. Even if an overestimation of the number densities is not desirable because it provides non-conservative values for nuclear safety application, the discrepancies are small enough to be neglected. Essentially there were no discrepancies between Eqs. (1b) and (4) for number densities of the rest nuclides.

In order to examine the effect of differences in hydrogen and oxygen number densities on nuclear criticalty, some hypothetical uranium nitrate solutions as is described in Table 4 were taken in this study. Nuclear criticality in terms of critical radius for these solutions was computed by using ANISN transport code[8] with Hansen-Roach sixteen group cross sections.[9]

The calculated results are tabulated in Table 5. The difference in the critical radius is of opposite sign to the difference in hydrogen, and the magnitude of the difference on the critical radius is less than or equal to the magnitude of the difference in the hydrogen number density.

5. Conclusion

The empirical formula derived in this study, $Q=1-0.3628C-0.0327H^+$, finds an application for determining readily water content in uranyl nitrate solutions which have uranium concentrations ranging from 0.004g/cc to 0.295g/cc and nitric acid normality from 1.00 to 5.06.

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