# First Experimentally Determined Thermodynamic Values of Francium: Hydration Energy, Energy of Partitioning, and Thermodynamic Radius

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Ⓢ Supporting Information

ABSTRACT: The Gibbs energy of partitioning of Fr^+ ion between water and nitrobenzene has been determined to be 14.5 ± 0.6 kJ/mol at 25 °C, the first ever Gibbs energy of partitioning for francium in particular and the first ever solution thermodynamic quantity for francium in general. This value enabled the ionic radius and standard Gibbs energy of hydration for Fr^+ to be estimated as 173 pm and −251 kJ/mol, respectively, the former value being significantly smaller than previously thought. A new experimental method was established using a cesium dicarbollide as a cation-exchange agent, overcoming problems inherent to the trace-level concentrations of francium. The methodology opens the door to the study of the partitioning behavior of francium to other water-immiscible solvents and the determination of complexation constants for francium binding by receptor molecules.
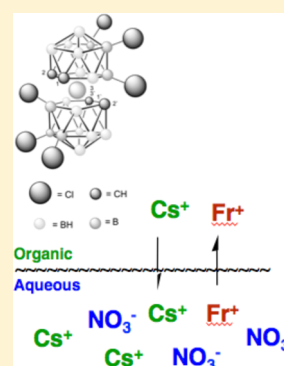
INTRODUCTION

Francium is the second-most scarce natural element on earth due to the short half-lives of all its isotopes (maximum 21.8 min, for ^{223}Fr).[1,2] The consequent experimental difficulties make it one of the least-studied elements of the periodic table. Yet textbook wisdom suggests that its behavior is rather well understood as an extension of the lower alkali metals,[3,4] in line with qualitative observations, most of them over half a century old.[5−7] With such reasoning as a working hypothesis, the current thermodynamic understanding of this element has relied exclusively on extrapolation from data on other metals.[8−11] While such empirical extrapolations have approximate predictive value, they are open to question.[12−14] Recently, curiosity about electronic properties, especially as influenced by relativistic effects, has made the study of francium primarily the domain of computational physicists and radioactive-beam spectroscopists.[15−17] Experimentally determined thermodynamic data are desirable to extend our knowledge of the alkali metals, test the conventional wisdom, and understand whether electronic effects might be reflected in its solution behavior.

An attractive experimental approach to realizing the above goals lies in determination of the partitioning behavior of the Fr^+ cation. Despite the troublesome short half-life of francium isotopes, radiometric methods allow measurement of precise distribution ratios, which can then be related to standard Gibbs energies of ion partitioning. Taking advantage of the routine availability of ^{225}Ac ($t_{1/2} = 10$ days), the parent of ^{221}Fr ($t_{1/2} = 4.8$ min),[18] we sought to develop a methodology for measuring the partitioning of Fr^+ ion between water and nitrobenzene.

Through reliable correlations, it was further sought to provide an improved and altogether new estimate respectively for the ionic radius of Fr^+ and its standard Gibbs energy of hydration.

Thermodynamic data obtained through extraction generally involve macro or micro quantities of the species of interest. In the case of ^{221}Fr, its half-life is so short that it needs to be created in situ from the decay of the ^{225}Ac parent. The concentration of francium in the extraction experiments is typically $\sim 10^{-14}$ M, which is considered an ultratrace level. In order to alleviate the issues of entrainment or extraction by impurities present in the system, we approached the determination of the Gibbs energy of partitioning for francium through the equilibria that govern the cation exchange between cesium and francium. Nitrobenzene was chosen as the water-immiscible diluent for its high polarity, which ensures complete ion dissociation in the organic phase. This diluent will be water-saturated at equilibrium as the results will be obtained via solvent extraction. The lipophilic "dicarbollide" anion (hexachloro bis(dicarbollyl)cobaltate) is a very large anion that has been used to extract cesium by cation exchange when used in its acidic form.[19] It will be a spectator ion in the nitrobenzene phase.
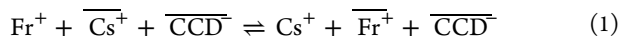
The overall equilibrium for the exchange is given by eq 1, since the system is fully dissociated in nitrobenzene, where overbars indicate organic-phase species and CCD^- is the dicarbollide anion. Thus, we have effectively achieved the

process in eq 2. The distribution ratio D_M for a metal is given as the ratio of its organic- to aqueous-phase molarities. Thus, the equilibrium constant for the exchange, K, is simply the ratio of distribution ratios for Fr and Cs. Activity coefficients for cesium and francium are very similar for this system; therefore, they cancel and consequently are not shown. Note that, in both aqueous and organic phases, concentrations of Cs and Fr are low enough for the Debye−Hückel term to be predominant in the activity coefficient expression. A similar approach is true for the organic phase) and therefore cancel. They are not shown.

$$Fr^+ + \overline{Cs^+} + \overline{CCD^-} \rightleftharpoons Cs^+ + \overline{Fr^+} + \overline{CCD^-} \qquad (1)$$

$$Fr^+ + \overline{Cs^+} \rightleftharpoons Cs^+ + \overline{F_r^+} \qquad (2)$$

$$K = \frac{[\overline{Fr^+}]}{[Fr^+]} \times \frac{[Cs^+]}{[\overline{Cs^+}]} = \frac{D_{Fr}}{D_{Cs}} \qquad (3)$$

The value of K should remain a constant over conditions where eq 1 holds, and that constant yields the $\Delta\Delta G°$ for Fr/Cs exchange between water and the organic phase:

$$\Delta\Delta G°_{Fr/Cs\,part,w\rightarrow o} = -RT\ln\left(\frac{D_{Fr}}{D_{Cs}}\right) \qquad (4)$$

In our experiments, cesium dicarbollide is dissolved at 1 mM in nitrobenzene and the solution contacted with increasing concentrations of aqueous cesium nitrate containing a spike of ^{225}Ac. The exchange between francium and cesium was followed by gamma-ray spectrometry.

The goal of the method is to determine the gamma activity of francium in the organic and aqueous phases at the instant when the two phases are no longer subject to mixing. Toward this endeavor, multiple counting results were obtained at different times. Since actinium is then absent in the organic phase (which was verified by analyzing the organic phase several hours after the phase separation for actinium content), francium decays according to its decay rate, allowing the calculation of its initial activity, $A_{Fr,i,org}$. Francium will have disappeared in part from the aqueous phase but regrows to reach the secular equilibrium with its much longer lived parent. An increase in counts over time occurs until reaching a plateau, allowing the calculation of the initial activity of francium in the aqueous phase. Several controls were implemented: First of all, the total activity of francium before contact with the organic phase was measured and was compared with the activity in the aqueous phase postcontact after the secular equilibrium was reached. These values agreed within ±5%. Also, the sum of the activity of francium in the organic and aqueous phases postextraction extrapolated to $t = 0$ compared satisfactorily to the total available activity, confirming the activity balance.

The experimental protocol had to be modified in order to address issues that had arisen due to the extremely low concentrations of francium and actinium present in the aqueous phase. It was discovered through the activity balance described above that the amount of actinium decreased in the aqueous phase. Since it was not extracted into the organic phase, it was assumed that it was partly adsorbed at the liquid−liquid interface. Therefore, the aqueous aliquots were no longer representative of the aqueous phase in equilibrium with the organic phase. This issue was solved by adding 0.01 mM of europium nitrate to the aqueous phase. It was demonstrated experimentally by adding ^{152}Eu to the aqueous phase that this trivalent cation was not extracted in this system. This amount

was sufficient to presumably displace the actinium from the interface and provide accurate measurements. The concentration of europium was varied by several orders of magnitude. The results for cesium and francium remained the same and a very low concentration was chosen to not modify the overall nitrate concentration. It was also discovered that the concentration of cesium dicarbollide present in the organic phase had to be equal to or lower than that for cesium nitrate in the aqueous phase. Without this restriction, francium distribution ratios started decreasing as soon as the CsCCD concentration exceeded the $CsNO_3$ concentration. The solubility of CsCCD in water was determined to be 0.015 mM, which could be considered as negligible when macro-quantities of salts are used, but must be taken into account when one of the ions is at 10^{-14} M. As the concentration of nitrate becomes lower than that of CsCCD, some dicarbollide anion is released into the aqueous phase, which starts competing with the exchange into the organic phase.

The chosen conditions therefore included an organic phase containing 1 mM of CsCCD in nitrobenzene and an aqueous phase containing variable concentrations of cesium nitrate and 10^{-5} M of $Eu(NO_3)_3$ in which were spiked ^{137}Cs (0.5 μCi/mL) and ^{225}Ac (10 μCi/mL).

As shown in Figure 1, francium is more extractable than cesium. The value of $\log D_{Fr}$ decreases with $\log[Cs^+]_{aq}$ with a
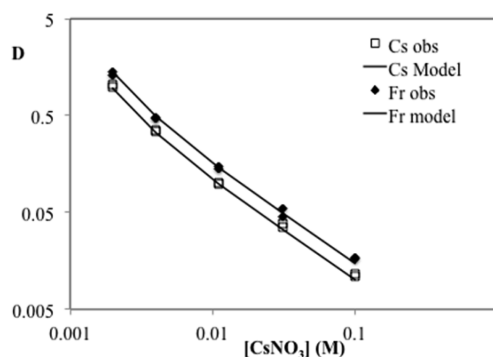

Figure 1. Francium and cesium distribution ratios as a function of aqueous $CsNO_3$ concentration. Conditions: organic phase containing 1 mM of CsCCD in nitrobenzene, aqueous phase containing variable concentrations of cesium nitrate and 10^{-5} M of $Eu(NO_3)_3$ and 5 μCi of $^{225}Ac/^{221}Fr$.

slope of −1, as expected based on eq 3. The value of $\log D_{Cs}$ decreases in parallel because of the fixed Cs concentration in the organic phase. The Fr and Cs distribution ratios were precisely modeled using the Fortran-based program SXLSQI[20] treating eq 1 as the sum of competing ion-pair extractions of CsCCD and FrCCD (see Supporting Information). Thus, the slight partitioning of CsCCD to the aqueous phase is exactly accounted for in the calculation.

On the basis of the modeling results as presented in Figure 1, the value of $\log_{10} K$ was determined to be 0.164 ± 0.011, which corresponds to a value of −0.926 ± 0.06 kJ/mol for $\Delta\Delta G°_{Fr/Cs\,part,w\rightarrow NB}$. The value $\Delta G°_{part,w\rightarrow NB}$ for cesium was previously determined to be 15.4 ± 0.5 kJ/mol.[21] Therefore, the value of the francium $\Delta G°_{part,w\rightarrow NB}$ is equal to 14.5 ± 0.6 kJ/mol. The uncertainty of this value predominantly reflects the uncertainty in the $\Delta G°$ of partitioning for Cs^+, whereas the $\Delta\Delta G°$ for the exchange is relatively precise. All data presented were acquired at 25 °C.

From the experimentally determined Gibbs energy of partitioning can be estimated the hydration energy of francium. In general, solvation energies monotonically become less negative across a series of ions with increasing ionic radius.[22] The standard Gibbs energy of partitioning from water to NB is therefore expected to correlate with the standard Gibbs energy of hydration.[22] Figure 2 shows the correlation between the
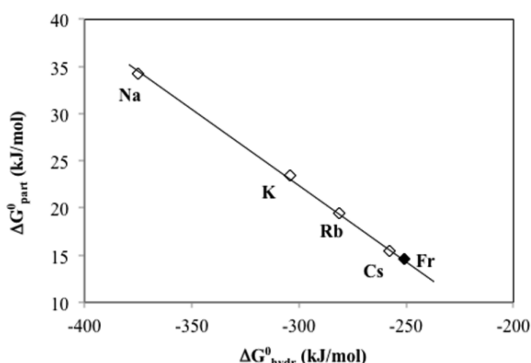
Figure 2. Hydration energies of alkali metals as a function of the corresponding Gibbs energy of partitioning.

standard molar Gibbs energy of partitioning of sodium, potassium, rubidium, and cesium[21] (open symbols) and their corresponding standard molar Gibbs energies of hydration.[23] The linearity of the relationship is remarkable (slope = -0.160 ± 0.004, $R^2 = 0.9987$) and can readily be extrapolated to francium. The corresponding value of $\Delta G^{\circ}_{hydr,Fr}$ is -251 ± 4 kJ/mol.

A similar extrapolation is possible to determine the thermochemical ionic radius of Fr^+ ion. As is well-known,[24] linear relationship exists between the Gibbs energy of partitioning of sodium, potassium, rubidium, and cesium and their corresponding radii as shown in Figure 3 (open symbols).
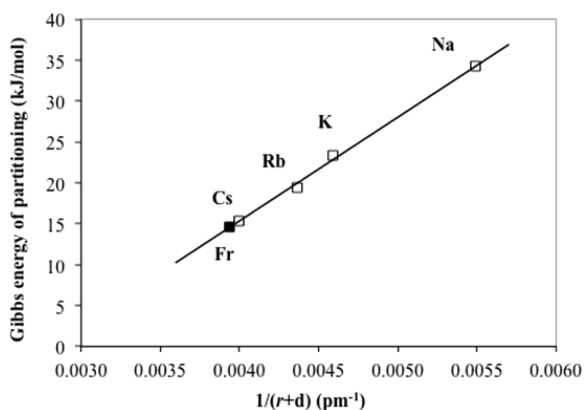
Figure 3. Gibbs energy of partitioning of alkali metals as a function of the corresponding cation radii. To the radius of the different alkali cations is added the conventionally accepted 80 pm (d).[24]

These points are used to establish a linear regression from which the value for francium can be calculated. The thermodynamic radius found for francium is 173 ± 1 pm, 7 pm smaller than originally proposed 60 years ago based on extrapolation from the ionic radii of other metals.[11] A phenomenon similar to the lanthanide contraction can be offered as a likely explanation.

In summary, we have obtained the first thermodynamic measurement for the Fr^+ ion, the significance of which is several-fold. First, we note that use of a measured thermodynamic value as a basis for estimation of the ionic radius and standard molar Gibbs energy of hydration improves the reliability of these estimates. Second, the estimates show that Fr^+ ion is closer to the size and behavior of Cs^+ ion than hitherto expected. On the basis of the intervals between K^+ and Rb^+ and Rb^+ and Cs^+, the change in radius and hydration energy in the interval Cs^+ to Fr^+ is significantly decreased. This observation is likely to have theoretical ramifications. Third, having these estimates will prove useful for multiple calculations of the properties of Fr^+ ion. From our own perspective, the methodology developed here will enable determination of the partitioning of Fr^+ to multiple water-immiscible solvents. Such values will then allow us to determine the homogeneous binding constants for Fr^+ ion to continue the fledgling coordination chemistry for this ion that we had previously established.[25] In addition, information about the thermodynamic behavior of this heavy alkali metal will be critical for predicting the chemical properties of element 119, the next element to be discovered and anticipated to be placed in the alkali series under francium.[26,27]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Corrections to take into account the [221]Fr decay while determining the activity of Fr in a given solution; parameters used in SXLSQI for the modeling of the Cs and Fr distribution ratios; linear regression of the distribution ratios obtained for cesium and francium along with the corresponding slopes; figure analogous to Figure 2 including lithium; figure analogous to Figure 3 including lithium. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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