

The elements are the longitude of node (Ω), longitude of perigee ($\tilde{\omega}$), inclination to ecliptic (I), eccentricity (e), equinox location (E), and obliquity of ecliptic (ϵ). Eccentricity e must be divided by 206265 to be returned to dimensionless units. These values are to be considered as observed corrections to the rates adopted in the Brown lunar theory (for Ω , $\tilde{\omega}$, I , e), the equinox implicit in the FK4 coordinate system (for E), and Newcomb's theoretical rate of change of obliquity (for ϵ).

In our opinion, the formal standard deviations given above may safely be doubled to obtain realistic error estimates, because of the difficulties inherent in making such error estimates from independent investigations. On that basis, we do not consider the rates for the inclination or the obliquity to be statistically significant. The solution for obliquity does not distinguish between Newcomb's theoretical obliquity motion ($\Delta\epsilon = 0$) and the observed value ($\Delta\epsilon = -0.3$) (4).

The rate of change of the eccentricity of the moon's orbit does appear to be statistically significant, although only marginally. Perhaps we have here an indication of the action of tidal friction on the shape of the moon's orbit, which contradicts the general assumption that tidal friction affects only the mean motion of the moon within observational accuracy.

The value $\Delta dE/dT$ represents the motion of the FK4 equinox relative to an ideal, or dynamical, equinox. By itself, it does not necessarily imply a correction to precession. However, it seems to be consistent with recent results (5), which imply a correction to lunisolar precession of +1.10 seconds per century, together with an equinox motion of $+1.20 \pm 0.11$ seconds per century.

The values of $\Delta\Omega$ and $\Delta\tilde{\omega}$ have been corrected for equinox motion by using the results found here for ΔE . Discordances between theoretical and observed values for these rates have been discussed by many authors, the most recent being Eckert (6). The corrections to the observed rates given here should help to resolve those discordances.

In particular, the parameters g' (mass distribution) and f (ratio of moments of inertia) discussed by Eckert would become $g' = +0.82$, $f = +0.65$, if the solution presented here is adopted. Such a g' value would require denser mass distribution near the lunar surface than at the moon's center.

Recent lunar orbiter results tend to fix g' near +0.60. If that value is correct, there is still a large, unexplained motion of the nodes of the lunar orbit of about -6.3 second per century, according to Eckert's results (6). If we also accept Baierlein's opinion (7), then the discrepancy is further increased by the amount of the geodesic precession and becomes -8.2 second per century.

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Helium Isotope Effect in Solution in Water and Seawater

Abstract. *The isotope effect in the solution of helium in water from 0° to 40°C has been determined by microgasometric measurements of the solubilities of pure helium-3 and helium-4. At 0°C helium-3 is less soluble than helium-4 in both distilled water and seawater by 1.2 percent. The observed fractionation factor is 0.988 ± 0.002 at 0°C and appears to decrease with increasing temperature at the rate of 0.0001 per degree Centigrade, although the existence of this trend is of limited statistical certainty. The measured isotope effect is in agreement with the ratio of helium-3 to helium-4 in surface ocean water reported by Clarke, Beg, and Craig.*

The recent discovery by Clarke *et al.* (1) of excess He^3 in the sea, attributed to primordial helium, focuses new attention on the importance of measuring the effect of isotopic fractionation in the solution of He^3 - He^4 mixtures in seawater. Similarly, the degree to which He^3/He^4 ratios in natural gases (2, 3) are affected by solubility interaction with groundwaters (4) depends upon the isotopic fractionation factor. Finally, data on isotopic effects in the solution of gases in water are of interest

with reference to the structure of water (5, 6). Therefore this report presents precise determinations of the differences between He^3 and He^4 solubilities at several temperatures in distilled water and in seawater as part of a more extensive series of rare gas solubility measurements made in this laboratory.

Solubility determinations were made by the Scholander microgasometric technique as used by Douglas (7) with minor modification (8). Pure He^3 and He^4 gas were used (9). After a simple temperature correction this method gives the Bunsen solubility coefficient, namely, the volume of gas (at standard temperature and pressure) absorbed per unit volume of liquid at the temperature of the measurement when the partial pressure of the gas is 1 atm.

Isotopic fractionation effects are reported in terms of the isotopic fractionation factor α , defined here as

$$\alpha = \frac{(\text{He}^3/\text{He}^4) \text{ aqueous phase}}{(\text{He}^3/\text{He}^4) \text{ gas phase}} = \frac{K_3}{K_4} = \frac{\beta_3}{\beta_4}$$

where K is the Henry's law constant and β is the measured Bunsen solubility coefficient. Thus, $(\alpha - 1) \times 10^2$ is the single-stage percentage enrichment of the He^3/He^4 ratio in the aqueous phase relative to that in the gas phase.

Values of β and $(\alpha - 1)$ for distilled water and for seawater with a salinity of 36.425 per mil are listed in Table 1. Values of $(\alpha - 1)$ calculated from the mean measured Bunsen solubility coefficients are given at various temperatures for each type of water. A standard error of 0.2 percent for each value of $(\alpha - 1)$ was calculated from the dispersion of the 52 individual solubility coefficient measurements. Systematic effects which do not cancel when the solubility ratio is taken are estimated to introduce an additional error of 0.1 percent in $(\alpha - 1)$.

If we compare the results for both types of water, the isotopic fractionation in seawater is, on the average, 0.2 percent greater than that in distilled water. The t -test and the rank sum test were used to evaluate the statistical significance of this difference. Both tests failed to establish a significant difference between values for distilled water and those for seawater at the 60 percent confidence level. Values of $(\alpha - 1)$ were therefore taken to be independent of salinity over the range studied.

The existence of a trend in $(\alpha - 1)$ with temperature is suggested by the observation that the values at 40°C show a greater fractionation than any of the values at lower temperature.

Table 1. Solubilities of He³ and He⁴ and calculated isotopic fractionation values for distilled water and seawater at various temperatures. Values shown in columns 2 and 3 are the mean of the number of measurements listed in parentheses; ranges shown are ± 1 standard deviation.

Temperature (°C)	Bunsen solubility coefficient $\times 10^3$		$(\alpha-1)$ (%)
	He ³	He ⁴	
	<i>Distilled water</i>		
0.60	9.254 \pm 0.026 (4)	9.355 \pm 0.004 (4)	-1.1
20.11	8.620 \pm 0.016 (4)	8.724 \pm 0.024 (6)	-1.2
40.14	8.574 \pm 0.019 (5)	8.713 \pm 0.036 (4)	-1.6
	<i>Seawater, salinity 36.425 per mil</i>		
0.07	7.655 \pm 0.012 (4)	7.771 \pm 0.025 (5)	-1.5
20.13	7.339 \pm 0.009 (4)	7.420 \pm 0.029 (4)	-1.1
40.46	7.346 \pm 0.028 (4)	7.488 \pm 0.015 (4)	-1.9

Since the Bunsen coefficients for He³ and He⁴ both pass through a minimum at around 30°C, an increase in fractionation might be explained by a greater mass dependence in the processes which govern solubility at temperatures above the minimum.

Without enough values of $(\alpha - 1)$ to justify a more complex treatment, the data were fitted to a linear least-squares regression line:

$$(\alpha - 1)\% = (-1.16 \pm 0.18) - (0.011 \pm 0.007)t$$

where t is the temperature in degrees Centigrade and the errors in the constants represent 1 standard deviation. The 0.28 percent standard deviation of the data about the line is in good agreement with the expected value of 0.3 percent. From the error in the second coefficient it is estimated that the existence of a trend in $(\alpha - 1)$ with temperature can be established only at the 80 percent confidence level.

Although the results show that no gross variations in the fractionation factor occur over the salinity and temperature range studied, further experimental work is needed to precisely establish the nature of such variations. At present $(\alpha - 1)$ for distilled water and seawater is best represented as -1.2 percent ± 0.2 percent at 0°C, with this value becoming more negative by 0.1 percent with each 10°C increase in temperature.

The results show that for helium the Henry's law constant is lower for the heavier isotope than for the lighter isotope. The same effect was found by Klots and Benson (6) for isotopes of oxygen and nitrogen, although the difference was only ~ 0.08 percent for both gases. A larger isotope effect would be expected for helium since there is a much larger percentage mass difference between its isotopes and because it is a monatomic gas.

Clark *et al.* (1) report that the He³/He⁴ ratio in their one sample of surface

ocean water is depleted by 1.8 percent ± 1.1 percent relative to the ratio in air, where the error quoted is ± 1 standard deviation. At the temperature of their sample (18°C), the results reported here predict a fractionation of -1.4 percent ± 0.2 percent and are therefore in good agreement with their work.

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References and Notes

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- The equilibration chamber was enlarged to contain approximately 10 ml of water, the constant temperature bath was improved, and procedures for degassing water and transferring gas were checked for air contamination by gas chromatography. The results have been corrected for the effect of the dissolution of the gas on the volume of the aqueous phase.
- The He³ used was supplied by Monsanto Research and was specified to be > 99.97 percent He with a He³/He⁴ ratio of 10^4 . Air Reduction reactor grade He specified to be > 99.99 percent He was used for the He⁴ measurements. Aldrich and Nier (2) found the He³/He⁴ ratio to be $< 10^{-6}$ in natural gas wells from which cylinder He is obtained. Gas chromatographic checks of the purity of these gases showed ≤ 0.025 percent and ≤ 0.01 percent air contamination for He³ and He⁴, respectively.
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Xenon Hexafluoride: Structure of a Cubic Phase at -80°C

Abstract. *The crystal structure of a cubic phase of composition XeF₆ has been determined at -80°C . There are no simple molecules in the complex structure which involves 1008 atoms distributed over 1600 positions per unit cell. Ions of XeF₅⁺ and F⁻ are associated in tetrameric and hexameric rings of point group symmetries $\bar{4}$ and $\bar{3}2$, respectively. The structure contains right- and left-handed conformations of both tetramers and hexamers. The handedness of the tetramers is disordered but the orientation is ordered. The handedness of the hexamers is ordered but the orientation is disordered.*

We here report the structure of a cubic phase of composition XeF₆. The properties of material of this composition pose unusual problems in all states of matter, whether gas, liquid, or solid (1). The multiplicity of symmetry relations in cubic space groups with their concomitant restrictions on possible spatial distributions suggests that a cubic phase should be the favored subject for study in the exceptional cases where the option is available.

In 1965 the existence of cubic XeF₆ was reported (2), with the probable space group $F\bar{4}3c$ or $Fm\bar{3}c$ and $a = 25.34 \pm 0.05$ Å (temperature not specified). We find that well-formed crystals of cubic XeF₆ invariably result when capillaries of FEP (fluorinated ethylene propylene copolymer) partly filled with XeF₆ are maintained at 18°C for several days. The sodium fluoride complexing method was used to prepare and purify XeF₆ (3). The FEP capillaries were prefluorinated with XeF₆ and heat-sealed after introduction of the specimens. The crystals give increasingly stronger x-ray reflections as the temperature is lowered. A temperature of -80°C was selected for intensity measurement as a compromise between quality of data and experimental difficulties. Details of the x-ray cryostat will be described elsewhere (4).

A crystal with dimensions 1 by 0.5 by 0.2 mm was used to measure 1023 unique reflections extending out to $d^* = 1.4$ Å⁻¹; Mo radiation, a scintillation counter, and the stationary crystal technique with 10-second counts and background counts on both sides of each reflection were used. With the high cubic multiplicity all measurements could be made with settings of high transmission. There were 487 reflections with peak-to-background ratios in