than a few tenths of a second of arc in diameter (*7*). Radio sources 3C 286 and 3C 287 are unresolved at a wavelength equal to 11 cm with a base line of $1.1 \times 10^6\lambda$; 3C 273B is unresolved at a wavelength equal to 6 cm with a base line of $2.1 \times 10^6\lambda$; and 3C 237 shows fringes characteristic of a double source at a wavelength equal to 21 cm with a base line of $6 \times 10^5\lambda$ (*8*).

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Oxygen Solubility in Sea Water: Thermodynamic Influence of Sea Salt

Abstract. *Precise measurements of the solubility of oxygen in sea water show that the solubility declines exponentially with increase in salt concentration according to the empirical Setschenow relation. The deviation from linearity is nearly 0.6 percent from the fitted straight-line relations of previous workers. Our experimental data reveal that, in contrast to the effect predicted by the Debye theory, the salting-out decreases with increasing temperature.*

In order to evaluate the influence of sea salt on the solubility of oxygen in water, the ratio of solubility (β) of oxygen in sea water to oxygen in distilled water was determined. As Henry's and Dalton's laws are obeyed at moderate pressures, β is independent of the partial pressure of oxygen with which the solutions are equilibrated. For inert gases in aqueous solutions, β decreases from unity upon the addition of moderate concentrations of electrolytes, this phenomenon being known as salting-out. Previous investigators (*1*) assumed that oxygen solubility depended linearly upon the concentration of sea salt.

The experimental procedure (*2*) entailed the simultaneous saturation of distilled water and sea water with water-saturated air at atmospheric pressure. The solutions were equilibrated concurrently in 12-liter rotating flasks immersed in a large thermostated bath capable of keeping the solutions within 0.01°C of a specific temperature. The air stream was presaturated with water at the temperature of the solutions; the air was blown gently over the top of the water samples in the flasks, whose rotation speed (22 rev/min) was such that no cavitation occurred. This method prevented the formation of bubbles and their attendant supersaturation.

When the solutions were saturated, the concentrations of dissolved oxygen were determined by Carpenter's modification (*3*) of the Winkler titration method. The titration was performed with a dead-stop amperometric end point; the end point was determined with two small platinum indicator electrodes having a potential difference of 182 mv. The ratio of the equivalent volume of titrant, necessary to titrate the oxygen in the sea water, to the corresponding volume for the distilled water gave β directly without one knowing either the partial pressure of oxygen in the air or the exact titrant concentration. In practice, both of these quantities were carefully evaluated so that solubility coefficients could be determined for the individual solutions. It is thought, however, that, whatever small systematic errors there may have been in the determinations of the solubility coefficients, these errors are likely to be canceled out in the measurements of β.

It was necessary to make a small correction in the directly obtained solubility ratios because of the effect of sea salt in lowering vapor pressure. For normal sea water the vapor pressure is about 2 percent lower than that for distilled water (*4*); as the vapor pressure amounts to 0.06 atm at 35°C, the increase in the oxygen partial pressure over sea water may amount to 0.12 percent.

Chlorinity determinations (*5*) were made with a Bradshaw-Schleicher conductivity bridge calibrated against Copenhagen standard water. Paquette (*6*) discussed the probable errors and assumptions inherent in use of this instrument, concluding that the probable error in the range of normal sea water is about 0.002 per mille Cl.

A total of 11 determinations were made, each being replicated from four to six times; they were made at temperatures ranging from 0° to 35°C and at sea-water chlorinities ranging from 6 to 30 per mille.

Determinations were replicated at a carefully controlled temperature of 22.02°C, for sea water of chlorinities near 6, 12, 18, 24, and 30 per mille, to show the salting-out effect unmodified by the pronounced temperature-dependence of the solubility; Fig. 1 shows a distinct regular deviation of β from the linear relation. The semilogarithmic plot shows that the data are well represented by

$$\beta = \exp\left[-k(t)\ \mathrm{Cl}\right] \qquad (1)$$

which is the empirical Setschenow (*7*) relation; it has been shown to be widely useful in representing salting-out data. Between 0 and 20 per mille Cl, the two curves of Fig. 1 never deviate from one another by more than 0.6 percent, so that it is not surprising that the nonlinearity escaped the previous workers, their determined solubility surfaces having a root-mean-square (standard) deviation of more than 0.6 percent.

Carpenter (see *8*) has recently confirmed the nonlinear dependence of solubility although he used a smoothing function that was quadratic in the chlorinity. Our data are well represented by the one-parameter exponential relation which has, in addition to simplicity, a thermodynamic basis. The difference in choice of smoothing functions probably derives from the fact that Carpenter was smoothing solubilities from a water-saturated atmosphere (that is, at a nonconstant partial pressure of oxygen) while we are smoothing Bunsen coefficients which may be expected to have a simpler functional representation.

To find the temperature dependence of k, values of the coefficient were calculated from the balance of the determinations; in Fig. 2 are also plotted the raw data of Fox (his 21 original unsmoothed sea-water solubilities combined with distilled-water values from his tables), Fox's smoothed curve (computed from his equation at 20 per mille Cl), and the smoothed curve of Truesdale *et al.* (their raw data not being available to us). It is immediately apparent that this kind of plot is a rather severe test of precision, for, as the spectacular temperature-dependence of the gas solubility obscures deviations, the weak temperature-dependence of the salting-out coefficient reveals them.

In its simplest form the Debye theory predicts

$$\log \beta = \frac{-AI}{DT} \tag{2}$$

where I is the ionic strength of the electrolyte, D is the dielectric constant of the solvent, T is the absolute temperature, and A is a measure of the effect of the solute nonelectrolyte on the dielectric constant of the solvent. To a first approximation, A is independent of temperature and salt concentration.

The data for water show that the product DT decreases with increasing temperature; therefore, according to the Debye theory, $-\log \beta$ should increase with temperature at a rate of about 0.1 percent per 1°C near room temperature. We find however that the salting-out coefficient decreases by about 7 percent per degree at low temperatures and by somewhat less at higher than room temperature. This decrease in the salting-out coefficient with increase in temperature has been observed for several other gases in various aqueous salt solutions (*9*). Clearly the simple Debye theory does not well apply to the data for the system under discussion.

The "internal pressure" concept has been explicitly developed (*9*) for the case of salting-out of a nonpolar nonelectrolyte. Not only has it been shown to predict the correct magnitude of the salting-out coefficient, but the observed temperature coefficient of k is also shown to decrease in magnitude above 25°C as we observed.

Randall and Failey (*10*) have shown that β is the reciprocal of the Henry's law activity coefficient of the dissolved gas in salt solutions. There is close relation between the excess partial molar free energy of solution and the activity

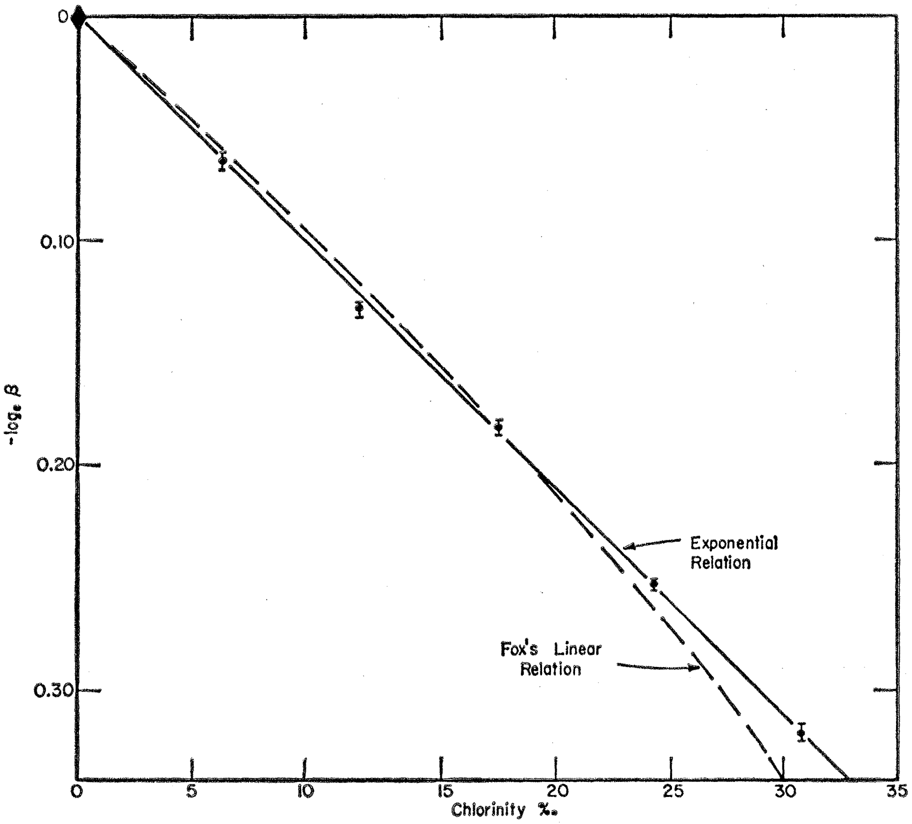

Fig. 1. Variation of the solubility ratio (β) with chlorinity; semilogarithmic plot; constant temperature, 22.02°C.

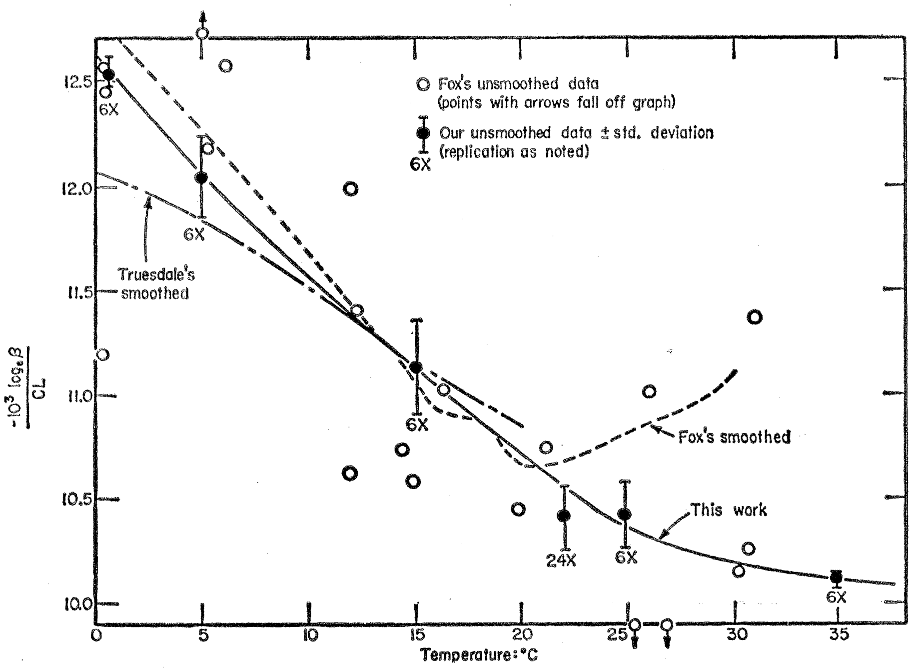

Fig. 2. The salting-out coefficient as a function of temperature.

Table 1. Excess partial molar thermodynamic quantities of solution for oxygen as a function of temperature. These represent the change of the total thermodynamic quantity resulting from the transfer of one mole of oxygen from a hypothetical solution, in which there is one mole of oxygen per liter, to a hypothetical molar solution of sea water of unit chlorinity. Unit Cl: unit chlorinity, sea salt.

Temperature (°C)	Cal (mole O_2)$^{-1}$ (unit Cl)$^{-1}$		Cal deg^{-1}(mole O_2)$^{-1}$ (unit Cl)$^{-1}$	
	$\Delta\tilde{G}_{O_2}^{xs}$	$\Delta\tilde{H}_{O_2}^{xs}$	$\Delta\tilde{S}_{O_2}^{xs}$	$\Delta\tilde{C}_{P_{O_2}}^{xs}$
0	6.92	24.3	0.064	(−0.7)
10	6.43	17.3	.038	(−0.7)
20	6.14	10.0	.013	(−0.7)
30	6.12	2.5	−0.012	(−0.8)

coefficient of the gas; in fact, the former may be avoided completely in thermodynamics by use of the latter.

$$\Delta\tilde{G}_{O_2}^{xs} = -RT \log \beta \tag{3}$$

Substituting the experimental relation of Eq. 1 in Eq. 3, we obtain

$$\Delta\tilde{G}_{O_2}^{xs} = RT\, k(t)\, \mathrm{Cl} \tag{4}$$

The determined excess partial molar free energy, as calculated from the experimental data by use of Eq. 4, was fitted to a temperature curve to yield smooth first and second derivatives:

$$k = -0.1288 + \frac{53.44}{T} - 0.04442 \log_e T + 7.145 \cdot 10^{-4}\, T \tag{5}$$

where T is the absolute temperature and k is given in reciprocal parts per thousand. From this smooth function the excess partial molar thermodynamic quantities were computed on a unit-chlorinity basis (Table 1). The root-mean-square (standard) deviation of the calculated excess free energy is within about 3 percent over a range of 35°C, or about 12 percent of the absolute temperature. The accuracy of the excess enthalpy and of the excess entropy, obtained from the temperature derivative, is of the order of 25 percent. Further differentiation to obtain the excess heat capacity cannot yield accurate values, but the calculated excess heat capacities are shown in parentheses in Table 1 to indicate merely that they are small negative quantities.

It is noted that the large exothermic (negative) heat of aqueous solution of oxygen (characteristic of N_2, Ar, and the other inert gases) is reduced significantly by the addition of even small amounts of sea salt. (Unit-chlorinity sea water is equal in ionic strength to a 0.037*M* solution of 1 : 1 electrolyte.) Frank and Evans (*11*) have suggested that the observed entropies of solution and the enormous positive partial molar heat capacities of solution for the inert gases are consistent with a model picturing the solute gas as producing a more highly structured order of the water molecules in its vicinity. The data of Table 1 suggest that addition of sea salt (mainly NaCl) results in disorganization of this induced structure.

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$$I = 0.00147 + 0.03592\,\mathrm{Cl} + 0.000068\,\mathrm{Cl}^2$$

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Bistatic-Radar Detection of Lunar Scattering Centers with Lunar Orbiter I

Abstract. *Continuous-wave signals transmitted from Lunar Orbiter I have been received on Earth after they have been reflected from the surface of the moon. The frequency spectrum of the reflected signals is used to locate discrete, heterogeneous, scattering centers on the lunar surface. The scattering centers are probably distinguished from the surrounding terrain by a higher surface reflectivity. Continuous-wave bistatic radar could provide an important new method for the study and mapping of planetary surfaces.*

The dispatch of space probes to the moon and planets has made it possible to study the surfaces of these objects with bistatic radar, that is radar with well-separated transmitter and receiver, one on Earth and the other carried into space on the probe. We here discuss a case where transmissions originated on the spacecraft, were reflected from the surface of the moon, and finally received on Earth. The opposite, or up-link, case is analytically equivalent and may be preferred for planetary studies because of the much greater power available from Earth-based transmitters.

We here present a preliminary analysis of the first bistatic-radar echoes obtained from a celestial body in order to (i) provide initial bistatic-radar evidence of the heterogeneity of the lunar surface, (ii) demonstrate the fact that the echo spectrum for continuous-wave illumination carries information from which a two-dimensional, radar-reflectivity map of the lunar surface can be constructed, and (iii) illustrate the potential of bistatic radar for eventual detailed mapping and radar-reflectivity studies of planetary surfaces.

The measurements described here were made on 12 October 1966, with the Lunar Orbiter I spacecraft. For the purposes of this experiment, the radiation from the spacecraft, which was emitted through an omnidirectional antenna, consisted essentially of a 100-milliwatt carrier at 2295 Mhz. The signal received on the ground consisted of this carrier and an image of the carrier reflected in the moon. Since the length of the direct path from the ground to the spacecraft varies at a different rate than does the length of