References and Notes

1. A. B. Reagan, *Kansas Acad. Sci. Trans.* **255**, pt. 3, 95–121 (1907).
2. J. H. Bretz, *Wash. Div. Mines Geol. Bull. No. 8* (1913).
3. J. E. Armstrong and W. L. Brown, *Geol. Soc. Amer. Bull.* **65**, 349–364 (1954).
4. D. J. Easterbrook, *Geol. Soc. Amer. Bull.* **74**, 1465–1484 (1963).
5. J. E. Armstrong, D. R. Crandell, D. J. Easterbrook, J. B. Noble, *Geol. Soc. Amer. Bull.* **76**, 321–330 (1965).
6. M. M. Leighton, *J. Geol.* **68**, 529–552 (1960).
7. J. C. Frye and H. B. Willman, *Geol. Soc. Amer. Bull.* **74**, 501–506 (1963).
8. G. M. Richmond, *Quaternary of the U.S.*, 7th INQUA Congr. Rev. Vol. (1965), pp. 217–230.
9. D. R. Mullineaux, H. H. Waldron, M. Rubin, *U.S. Geol. Survey Bull. 1194-0* (1965).
10. D. R. Crandell, *Quaternary of the U.S.*, 7th INQUA Congr. Rev. Vol. 353 (1965), pp. 341–353.

21 January 1966

Trace Element Partition Coefficient in Ionic Crystals.

Abstract. *Partition coefficients of monovalent trace ions between liquids and either solid $NaNO_3$ or KCl were determined. The isotropic elastic model of ionic crystals was used for calculating the energy change caused by the ionic substitutions. The observed values of partition coefficients in KCl are in good agreement with calculated values.*

Recently, Masuda and Matsui (*1*) suggested a possible picture of the evolution of the earth's lithosphere on the basis of rare-earth element partition patterns. The theory requires a quantitative knowledge of trace element partition between crystallized minerals and their mother melts. The well-known Goldschmidt's rule, which predicts trace element partition qualitatively in terms of ionic radii, is not adequate for their purposes. Difference in chemical properties between elements complicates making the rule quantitative; but some simplified treatment could be applied to the series of chemically similar elements, provided that the difference between them in chemical properties is neglected. I now report the quantitative treatment of the trace element partition in one of the most idealized cases, that of the ionic crystals, based on the theory of lattice defects.

Table 1. Trace element partition coefficients in $NaNO_3$ and KCl.

Element	Ionic radius* (Å)	Partition coefficient
	$NaNO_3$	
Na	0.98	(1)
Ag	1.13	7.5×10^{-1}
K	1.33	2.5×10^{-1}
Rb	1.49	2.5×10^{-2}
Cs	1.65	4.8×10^{-4}
	KCl	
K	1.33	(1)
Rb	1.49	7.9×10^{-1}
Cs	1.65	3.4×10^{-1}

* Ionic radii given by Goldschmidt.

Table 2. Calculated and observed value of the energy change of trace element substitution in KCl. Theoretical values are calculated with use of ionic radii of Goldschmidt.

Element	$\epsilon^2(1 + \epsilon/\gamma)$	$U_{\text{calc.}}$ (cal/mol)	$U_{\text{obs.}}$ (cal/mol)
Rb	0.014	500	510
Cs	.060	2200	2300

Partition coefficients of trace amounts of Ag, K, Rb, and Cs in $NaNO_3$, and of Rb and Cs in KCl, between liquid (molten salt) and solid (crystal) phases have been determined by the method of partial crystallization or of zone melting.

Partition coefficients, except that of Ag in $NaNO_3$, were determined as follows. Reagent grade $NaNO_3$ or KCl was mixed with known amounts of trace material and packed in a Pyrex or quartz tube (about 1 cm in diameter). The tube was mounted in the furnace (Fig. 1*a*). The temperature of the furnace was controlled slightly above the melting point of the main component material. The tube was lowered at a rate of 0.001 to 3 cm per hour until a few tenths of the total liquid phase had crystallized. The crystallized portion comprised about one-tenth of the initial weight of the material for analysis. The Rb and Cs were analyzed by radioactive tracers, Rb^{86} and Cs^{137}, and K was analyzed by frame photometry.

The partition coefficient of Ag in $NaNO_3$ is determined by the method of zone melting. The $NaNO_3$ is melted in a crucible and poured into a Pyrex tube. A small amount of $AgNO_3$ is placed above the $NaNO_3$ in the tube. The molten zone (about 1 cm) produced by a small ring heater was moved from top to bottom at a rate of 0.3 to 3 cm per hour. The crystal Ag in $NaNO_3$ thus formed was analyzed by ethylenediaminetetraacetate titration on each piece of crystal, cut to about 1 cm long. The partition coefficient is calculated from the slope of the straight line in Fig. 2.

The partition coefficients of Ag, K, Rb, and Cs in $NaNO_3$ are independent of the rate of crystal growth below 0.3 cm/hr (Fig. 3). The partition coefficients of Rb and Cs in $NaNO_3$ are constant for variations of the trace ion concentration below 10^{-2} and 10^{-4} mol/mol, respectively (Fig. 4). At higher concentrations, reproducible values of the partition coefficients have not been obtained. The observed values of the partition coefficients in KCl and $NaNO_3$ decrease regularly with increasing ionic radius (Table 1).

In order to calculate the partition

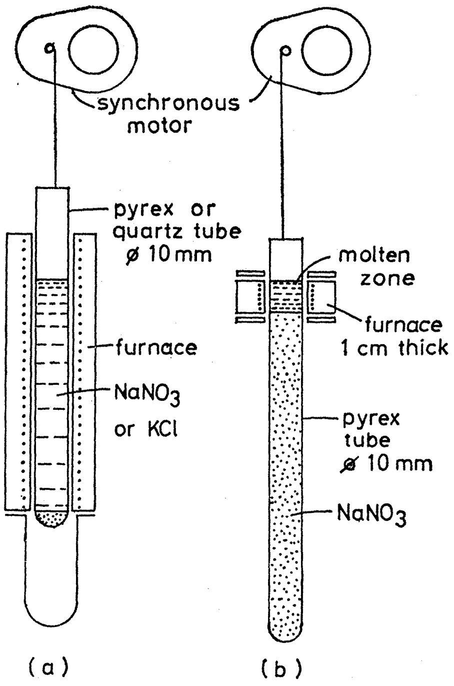

Fig. 1. Apparatus for determining partition coefficients. Arrangement of furnace and column for (*a*) partial crystallization and (*b*) zone melting.

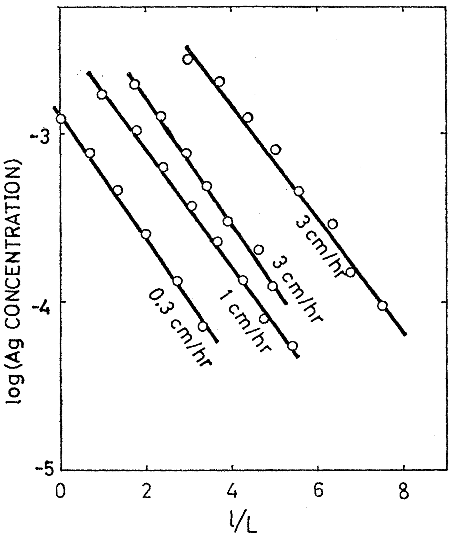

Fig. 2. Silver concentration plotted against *l/L*, where *L* is the width of molten zone, *l* is the position of the piece of crystal measured from the upper end. *D* is calculated from the equation $\log(C/C_0) = 0.4343 \cdot D(l/L)$, where *C* and C_0 are the concentrations of Ag at l and l = 0, respectively.

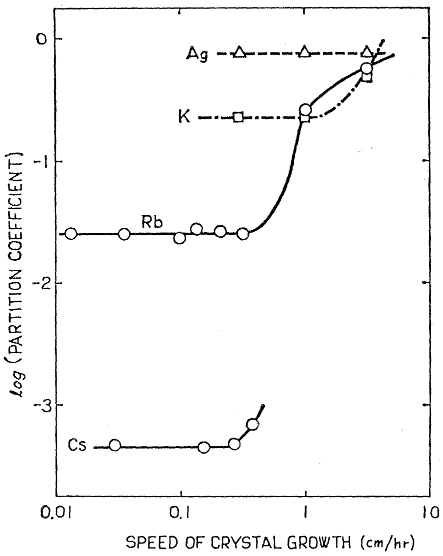

Fig. 3. Partition coefficients in $NaNO_3$ versus the speed of crystal growth. The speed of crystal growth is measured by the rate of the movement of the boundary between the two phases.

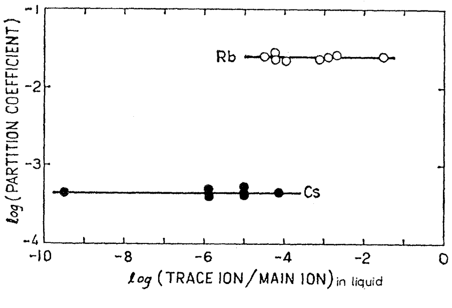

Fig. 4. Partition coefficients in $NaNO_3$ plotted against trace element concentration in initial liquid.

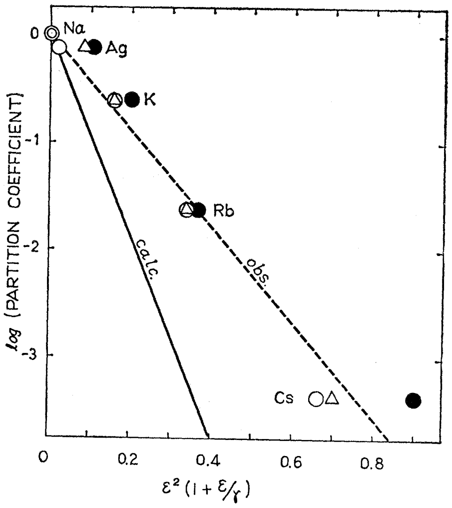

Fig. 5. Effect of ionic radii on partition coefficients in $NaNO_3$. Values are given for ionic radii of Goldschmidt, Pauling, and Ketelaar (*4*). Open circles, Goldschmidt data: closed circles, Pauling data; open triangles, Ketelaar. Theoretical line is calculated with the value of $T = 600°K$, and on the assumption that $\kappa = 4.4 \times 10^{-12}$ cm²/dyne at 600°K and $\sigma = 0.25$.

coefficients theoretically, we shall treat a system in which liquid (molten salt) and solid (crystal) phases are in equilibrium with each other. The free energy, G, of this system equals $H - TS$, where H, T, and S are the enthalpy, temperature, and entropy of this system, respectively. The concentration-dependent terms of the entropy of the liquid phase, S_1, and of the solid phase, S_c, are approximated to

$$S_1 = kT \ln(1/N_a!\,N_b!) \qquad (1a)$$

$$S_c = kT \ln(M!/M_a!\,M_b!) \qquad (1b)$$

where k is Boltzmann's constant, N and M are the number of ions in liquid and solid phases, respectively, and the subscripts a and b denote principal and trace components, respectively. Considering that G is a function of M_b, we can adopt the condition for the chemical equilibrium

$$(\partial G/\partial M_b)_p = (\partial H/\partial M_b)_p - T(\partial S/\partial M_b)_p = 0 \qquad (2)$$

for this system. The term $(\partial G/\partial M_b)_p$ is the free energy change provided by the substitution of an ion of the main component in solid phase by an ion of a trace component in liquid phase at constant temperature and pressure. In Eq. 2

$$(\partial H/\partial M_b)_p = (\partial E/\partial M_b)_p + p(\partial V/\partial M_b)_p \qquad (3)$$

where $(\partial E/\partial M_b)_p$ and $(\partial V/\partial M_b)_p$ are the internal energy and the volume changes of the substitution, respectively, and p is the pressure. Under ordinary experimental conditions, $p(\partial V/\partial M_b)_p$ is negligibly small compared with $(\partial E/\partial M_b)_p$, then the condition of the equilibrium is approximated to

$$(\partial E/\partial M_b)_p - T(\partial S/\partial M_b)_p = 0 \qquad (2')$$

From Eqs. 1 and 2′ we find

$$kT \ln D = -(\partial E/\partial M_b)_p \qquad (4)$$

where D is $(M_b/M_a)/(N_b/N_a)$ which is approximated to the partition coefficient, the ratio of concentrations of the trace ion between the two phases, when a and b are the main and trace components, respectively.

Here, we assume $(\partial E/\partial M_b)_p$ is the potential energy of strain which is computed as an energy required when a sphere of homogeneous isotropic material of radius $r_0(1 + \epsilon)$ is forced into a spherical hole of radius r_0 in an infinite block of the same material. The substitution of an ion caused the elastic displacement $\mathbf{u}$ (*2*),

$$\mathbf{u} \begin{cases} = A\mathbf{r} & \text{for } r \leqq R \\ = B\dfrac{\mathbf{r}}{r^3} = -B\,\mathrm{grad}(1/r) & \text{for } r \geqq R \end{cases} \qquad (5)$$

where A and B are constants, and R is the boundary between the substituted sphere and the outer material. From the condition that the outward and inward forces are balanced at the boundary, R is calculated to be $r_0(1 + \epsilon/\gamma)$, where $\gamma = 3(1 - \sigma)/(1 + \sigma)$, and σ is the Poisson's ratio of this elastic material (*2*). From this model, we can calculate the energy density $W(r)$ in the solid after the substitution (*3*):

$$W(r) \begin{cases} = \dfrac{9\epsilon^2(\gamma - 1)^2}{2\kappa\gamma^2}\dfrac{1}{(1 + \epsilon/\gamma)^2} & \text{for } r < R \\ = \dfrac{3\epsilon^2(\gamma - 1)r_0^6}{2\kappa\gamma^2 r^6}(1 + \epsilon/\gamma)^4 & \text{for } r > R \end{cases} \qquad (6)$$

where κ is the compressibility of the material. Integration of $W(r)$, multiplied by $4\pi r^2 dr$, from 0 to R, and R to ∞, respectively, yields

$$U_1 = \frac{6\pi r_0^3(\gamma - 1)^2}{\kappa\ \gamma^2}\,\epsilon^2\,(1 + \epsilon/\gamma) \qquad (7a)$$

$$U_2 = \frac{6\pi r_0^3(\gamma - 1)}{\kappa\ \gamma^2}\,\epsilon^2\,(1 + \epsilon/\gamma) \qquad (7b)$$

and

$$U = U_1 + U_2 = \frac{6\pi r_0^3(\gamma - 1)}{\kappa\ \gamma}\,\epsilon^2(1 + \epsilon/\gamma) \qquad (8)$$

Finally, the partition coefficients are

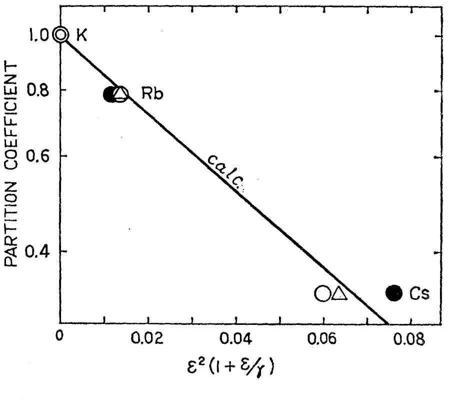

Fig. 6. Effect of ionic radii on partition coefficients in KCl. Values are given for ionic radii of Goldschmidt, Pauling, and Ketelaar. Symbols as in Fig. 5. Theoretical line is calculated with the value of $T = 1100°K$, and on the assumptions that $\kappa = 7.9 \times 10^{-12}$ cm²/dyne (*5*) at 1100° K, and $\sigma = 0.25$.

calculated by combining Eqs. 2′ to 8;

$$\ln D = -U/kT \qquad (9)$$

From Eq. 9, one finds ln D is linear with $\epsilon^2\ (1 + \epsilon/\gamma)$. By plotting the observed values of D logarithmically against $\epsilon^2\ (1 + \epsilon/\gamma)$. reasonably straight lines are obtained (Figs. 5 and 6). The observed values for KCl are in good agreement with the calculated values (Fig. 6 and Table 2). The case of $NaNO_3$ presents the straight line in Fig. 5, but the "observed" line disagrees considerably from the calculated one.

The model discussed is primarily an application of that presented in the theory of lattice defects (*2*). This model can be applied only in the case where the substituting ion is larger than the host ion. The experimental evidence suggests that this model can be used for the approximate calculation of trace element partition coefficients in ionic crystals. The calculation could also be applied to the distribution of the chemically similar trace elements, such as rare-earth elements, in minerals to provide a relation between the partition coefficients and the ionic radii.

HIROSHI NAGASAWA
Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo, Japan

References and Notes

1. A. Masuda and Y. Matsui, *Inst. Nucl. Study, Univ. Tokyo INSJ-53*, 22 pp.; *Geochim. Cosmochim. Acta*, in press.
2. J. D. Eshelby, *J. Appl. Phys.* **25**, 255 (1954).
3. For example, C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1953), pp. 85–102.
4. J. A. A. Ketelaar, *Chemical Constitution* (Elsevier, Amsterdam, 1958), pp. 28–29.
5. O. Madelung and R. Fuchs, *Ann. Phys.* **65**, 289 (1921); J. C. Slater, *Phys. Rev.* **23**, 488 (1924).
7. I thank Professors K. Kigoshi, A. Okawa, and Y. Nakagawa for their advice and encouragement. Supported by grants of Matsunaga Science Foundation.

9 March 1966

■

Reversible Combination of Carbon Monoxide with a Synthetic Oxygen Carrier Complex

Abstract. *Chlorocarbonyl-*bis*(triphenylphosphine)iridium(I), in solution, reacts reversibly with carbon monoxide under normal conditions, one molecule per metal atom. Formation of a 1 : 1 metal complex—CO adduct is verified by CO absorption measurements and the infrared spectrum of the adduct measured* in situ. *The spectrum suggests that the metal—C—O bonding is of the type found in conventional metal carbonyl.*

Although the reversible combination of carbon monoxide with the iron atom in hemoglobin and in related natural molecules has been extensively investigated (*1*), there appear to be no previously reported examples of *synthetic* transition metal complexes reacting in the same manner (*2*). The discovery of reversible oxygenation (*3*) of a synthetic metal complex, chlorocarbonyl-*bis*(triphenylphosphine)iridium(I) (*4*), shown in equation 1 (*5*),

$$[IrCl(CO)(Ph_3P)_2] + O_2 \rightleftarrows [O_2IrCl(CO)(Ph_3P)_2] \qquad (1)$$

immediately led us to consider other possible analogies between this inorganic system and biological oxygen carriers. As a result of these efforts, I wish to report the reversible carbonylation of the same parent compound,

$$[IrCl(CO)(Ph_3P)_2] + CO \underset{k_1}{\overset{k_2}{\rightleftarrows}} [(CO)IrCl(CO)(Ph_3P)_2] \qquad (2)$$

and the probable molecular configuration of the carbon monoxide adduct as deduced from gas absorption and spectroscopic measurements, structural properties of other adducts of the carrier complex, and a reported study of CO exchange in related metal complexes (*6*).

When a solution of $[IrCl(CO)(Ph_3P)_2]$ in benzene, toluene, or chloroform is flushed with carbon monoxide at room temperature and atmospheric pressure, the characteristic yellow color of the complex disappears, and the solution becomes nearly colorless within minutes. When the CO is allowed to escape from the solution, the original color reappears rapidly, and yellow crystals of the starting material can be recovered by precipitation with alcohol or by evaporation of the solvent. The CO adduct, $[(CO)IrCl(CO)(Ph_3P)_2]$, can be synthesized in white crystalline form by evaporating to dryness a CO-saturated solution of the metal complex in chloroform by means of a vigorous flow of carbon monoxide through the solution at room temperature. Both the crystals and the solutions of the adduct appear to be stable in an atmosphere of CO. Exposure to air causes both the reverse reaction (Eq. 2) and a reaction of the adduct with oxygen (*7*).

Volumetric measurements of carbon monoxide uptake by the parent compound in toluene solution indicate a 1 : 1 attachment of CO to the metal complex. At 16°C and 700 mm-Hg of CO (constant), the equilibrium concentration of the adduct is 93 mole percent of the total iridium concentration present in solution (1.87×10^{-3} mole/liter), and the value of the equilibrium constant (K_C) is 1.91×10^5 liter $mole^{-1}$ (*8*). Under the same conditions, the rate constant for the bimolecular synthetic reaction, k_2, is 43.4 liter $mole^{-1}$ sec^{-1}; for the dissociative reaction, calculation from K_C and k_2 gives $k_1 = 2.27 \times 10^{-4}$ sec^{-1}, the reverse rate constant (Eq. 2). Repeated cycling of carbonylation-decarbonylation does not measurably affect the pertinent properties of the reacting complexes. In a quantitative experiment, after the CO-uptake measurement the gas was completely removed from the system which was then resaturated under the original conditions (16°C, 700 mm-Hg of CO); the results of the two absorptions were identical.

The data of the infrared spectra of the CO adduct are given in Table 1 (*9*), together with those for the parent compound which are listed for comparison. The spectrum of the crystalline adduct, measured immediately after it was synthesized, showed no absorption bands attributable to the starting material. After 20 minutes in air, the appearance of the 1956 cm^{-1} band (Table 1) indicated that some desorption of CO had occurred, and after 40 hours, about one-half of the sample had been converted to the oxygen adduct $[O_2IrCl(CO)(Ph_3P)_2]$ (*7*).

The solutions of the CO adduct to be measured were prepared in the absence of oxygen, and a CO pressure of 1 atm or more was maintained above the solution in the infrared cell as the spectrum was obtained. Under these conditions, the presence of the parent compound was not detectable. After 5 days under carbon monoxide, the same solution gave a spectrum that was essentially identical with the original.

The interpretation of the infrared spectrum of the CO adduct is related to the coincidental fact that the parent compound $[IrCl(CO)(Ph_3P)_2]$ already contains one carbon monoxide ligand. Hence, the adduct is expected to repre-