Solubility of Noble Gases in Molten Fluorides

In Lithium-Beryllium Fluoride

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THIS investigation is part of a systematic study of the solubilities of gases in molten salts. Previous work from this laboratory described measurements of the solubility of noble gases (*1, 6*) in various molten fluoride mixtures over the temperature interval 600° to 800° C. This work concerned the following solvents: $NaF\text{-}ZrF_4$ (53–47 mole %), (*6*), $NaF\text{-}ZrF_4\text{-}UF_4$ (50–46–4 mole %), (*6*), and the ternary eutectic mixture of LiF–KF–NaF (*1*). The solubility behavior of the noble gases was correlated by equating the free energy of solution of the gas to the free energy of formation of holes which were assumed to be of the same size as the gas molecules in a continuous fluid having the same surface tension as the solvent (*1*). This approach yielded solubility values which are in good agreement with the experimental results.

The present investigation describes the results obtained on the measurement of solubility of He, Ne, Ar, and Xe in a mixture of $LiF\text{-}BeF_2$ (64–36 mole %) at pressures from 1 to 2 atm. at 500°, 600°, 700°, and 800° C. For xenon the experiments were performed at 600°, 650°, 700°, and 800° C., because of its extremely low solubility at 500° C. The experimental measurements are also compared with the calculated solubilities in this solvent, using experimental values of the surface tension (*3*). In addition, the solubilities previously calculated in the LiF-KF-NaF ternary eutectic using estimated surface tensions (*1*) have been recalculated from experimentally determined values of surface tension which have lately become available (*4*) and the results are presented.

EXPERIMENTAL

The noble gases used were obtained in cylinders from commercial sources. Helium was obtained from the Bureau of Mines at Amarillo, Tex.; Ne, Ar, and Xe were obtained from the Linde Co. All gases were shown by mass spectrometric analysis to exceed 99.9% purity. The molten fluoride mixture was prepared with reagent grade LiF and with BeF_2 obtained from The Beryllium Corp. of America, which met specifications of purity of 99.5 ± 0.5%. The fluorides were mixed in proper proportions and purified in a closed nickel system at 800° C. by alternate sparging with anhydrous HF and H_2. The resulting mixture was transferred under pressure of He to the solubility apparatus without exposure to the atmosphere. Chemical analyses of samples of the liquid obtained during the transfer operation yielded the following data:

$LiF\text{-}BeF_2$ (64–36 Mole %)

	Weight %	
	Theoret.	Obsd.
Li	13.15	13.3
Be	10.25	9.6
F	76.60	77.0
Fe	0	675[a]
Ni	0	195[a]
Cr	0	95[a]

[a] Parts per million.

The apparatus and procedure are identical to those described in previous publications (*1, 6*).

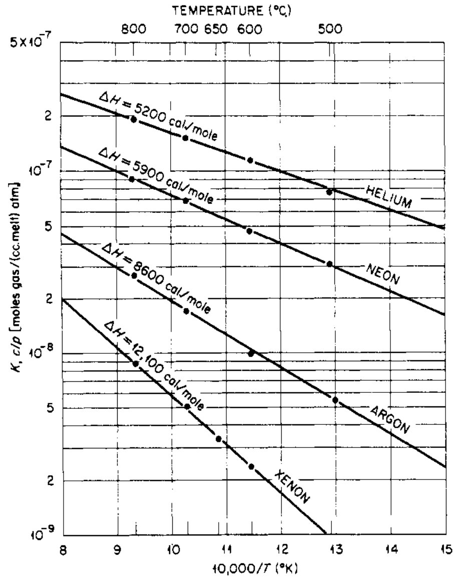

Figure 1. Temperature dependence of solubilities of noble gases in $LiF\text{-}BeF_2$ (64–36 mole %)

RESULTS

The solubilities and Henry's law constants for He, Ne, Ar, and Xe in molten $LiF\text{-}BeF_2$ (64–36 mole %) at the different temperatures investigated are shown in Table I. Figure 1 is a plot of Henry's law constants as functions of temperature. The solubility values could be duplicated in separate experiments to about ± 5%. The solubility values are in moles of gas per cubic centimeter of solvent and may be converted to other units as desired by use of solvent densities calculated from the equation (*2*):

$$\rho(\text{g./cc.}) = 2.09 - 2.7 \times 10^{-4} t^\circ \text{ C.}$$

DISCUSSION

The solubilities of all the gases studied in the present investigation obey Henry's law within the experimental precision of ± 5% and increase with increasing temperature and with decreasing molecular weight (or atomic radius) of the gas. The enthalpies of solution of the gases are positive and increase with increasing atomic weight (radius). Similar behavior has been observed previously at this laboratory regarding noble gas solubilities in other molten fluoride mixtures (*1, 6*). The temperature dependence of the solubility of noble gases in molten fluorides is the reverse of that exhibited by HF (*7*) and by BF_3 (*8*) in similar solvents. The solubilities of the latter gases decrease with increasing temperature and have negative enthalpies of solution.

Values of the enthalpies and standard entropy changes of solutions of noble gases in the $LiF\text{-}BeF_2$ solvent are listed in Table II with the corresponding values in other solvents. It may be observed (by comparing the ΔH and $T\Delta S$ values) that changes obtained in the $LiF\text{-}BeF_2$ mixture do not agree with the term $T\Delta S$ estimated from an ideal gas expansion, although the agreement was good

Table I. Solubility of Helium, Neon, Argon, and Xenon in LiF-BeF_2(64–36 Mole %)

Temp., ° C.	Pressure, Atm.	Solubility × 10^8, Moles/Cc. Melt		K = C/P × 10^8, (Moles) / (Cc. Melt) (Atm.)
		(Helium)		
500	1.009	7.46		7.39
	1.521	11.46		7.53
	1.996	15.08		7.56
			Av.	7.49 ± 0.07
600	1.103	11.74		11.59
	1.570	18.76		11.95
	2.107	22.40		11.11
			Av.	11.55 ± 0.39
700	1.004	14.81		14.75
	1.526	23.75		15.56
	1.963	28.41		14.47
			Av.	14.93 ± 0.42
800	0.996	19.39		19.47
	1.520	29.63		19.49
	1.978	38.65		19.49
			Av.	19.48 ± 0.01
		(Neon)		
500	1.032	3.130		3.033
	1.030	3.025		2.963
	1.509	4.849		3.213
	2.010	6.327		3.142
			Av.	3.088 ± 0.090
600	1.004	4.619		4.601
	1.497	6.939		4.635
	1.991	9.243		4.642
			Av.	4.626 ± 0.013
700	1.021	6.852		6.711
	1.499	10.407		6.943
	1.983	13.387		6.751
			Av.	6.802 ± 0.094
800	1.003	9.265		9.237
	1.509	13.451		8.914
	1.991	17.670		8.875
			Av.	9.009 ± 0.152
		(Argon)		
500	0.996	0.562		0.56
	1.014	0.523		0.52
	1.024	0.519		0.51
	1.489	0.755		0.51
	1.500	0.855		0.57
	1.960	1.041		0.53
	1.964	1.088		0.55
			Av.	0.54 ± 0.02
600	0.984	1.001		0.98
	0.996	0.949		0.95
	0.997	1.001		1.00
	1.013	1.046		1.03
	1.513	1.466		0.97
	1.513	1.417		0.94
	1.971	1.927		0.98
	1.987	1.919		0.97
			Av.	0.98 ± 0.02
		(Argon)		
700	0.989	1.596		1.61
	0.996	1.736		1.74
	1.008	1.566		1.55
	1.025	1.582		1.54
	1.249	1.960		1.57
	1.479	2.688		1.82
	1.513	2.485		1.64
	1.514	2.697		1.78
	1.934	3.444		1.78
	1.954	3.618		1.85
	1.967	3.337		1.70
			Av.	1.69 ± 0.10
800	0.993	2.628		2.65
	0.999	2.612		2.62
	1.020	2.696		2.64
	1.239	3.227		2.60
	1.476	3.908		2.65
	1.499	3.888		2.59
	1.532	4.077		2.66
	1.532	4.242		2.77
	1.922	5.260		2.74
	1.967	5.145		2.62
	2.008	5.007		2.50
			Av.	2.66 ± 0.06
		(Xenon)		
600	0.988	0.231		0.233
	1.487	0.343		0.231
	1.979	0.469		0.237
			Av.	0.233 ± 0.002
650	1.030	0.330		0.321
	1.474	0.483		0.328
	1.962	0.687		0.350
			Av.	0.333 ± 0.011
700	1.000	0.512		0.512
	1.483	0.782		0.527
	1.970	0.944		0.485
			Av.	0.505 ± 0.020
800	1.020	0.897		0.880
	1.464	1.232		0.842
	1.954	1.697		0.868
			Av.	0.863 ± 0.021

in the case of the two other solvents (*1*, *6*). The entropies of solution, $\Delta S°$, shown in Table II, may be readily calculated by subtracting the $T\Delta S$ values which appear in the table and dividing by the temperature (1000° K). The $\Delta S°$ thus calculated is based on standard states of equal concentration of gas in solution and in the gas phase. This turns out to be a convenient choice of standard states, because it eliminates the trivial contribution (to the standard entropy of solution) which arises from the expansion or compression effects. The $\Delta S°$ is by this choice purely a function of the environment of the gas atoms.

Table II. Enthalpy and Entropy Changes on Solution of Noble Gases in Molten Fluoride Mixtures at 1000° K.

Solvent	Gas	ΔH, Cal./Mole	Ideal Gas Expansion, $T\Delta S$, Cal./Mole	$\Delta S°$, E.U.
LiF-BeF_2 (64–36 mole %)	He	5,200	8,600	−3.4
	Ne	5,900	10,100	−4.2
	Ar	8,600	12,800	−4.2
	Xe	12,100	15,200	−3.1
NaF-KF-LiF (11.5-42-46.5 mole %)	He	8,000	8,300	−0.3
	Ne	8,900	9,900	−1.0
	Ar	12,400	12,500	−0.1
NaF-ZrF_4 (53–47 mole %)	He	6,200	7,200	−1.0
	Ne	7,800	8,200	−0.4
	Ar	8,200	9.700	−1.5
	Xe	11,100	11,200	−0.1

The negative ΔS° values for the LiF-BeF$_2$ mixtures are much greater than those corresponding to the other solvents. This comparison shows that the environmental conditions of the gas atoms in the LiF-BeF$_2$ solvent differ considerably from those in the other solvents. To pursue this point further, it is convenient to introduce a brief discussion of predicted behavior.

An equation (*1*) expressing Henry's law constant as a function of the surface tension of the liquid, the radius of a spherical gas atom, and the temperature is

$$K_c = \exp\left(-\frac{18.08\, r^2 \gamma}{RT}\right) \qquad (1)$$

Henry's law constant in Equation 1 is expressed as the ratio of gas concentration in solution to that in the gas phase, or $K_c = K(RT)$. The radius of the gas atom, r (expressed in Angstrom units), is assumed to be the same as in the solid state (*5*). The surface tension, γ (in ergs per square centimeter), was determined experimentally for each solvent by other investigators (*3, 4*). Comparisons between calculated and experimental Henry's law constants are given in Table III.

If the estimated hole size (r, in Equation 1) were too low, the predicted solubility would be too high. This appears to be the case in the majority of instances covered by Table III. Aside from this discrepancy, the model gives a fairly accurate description of the noble gas solubility behavior in the solvents studied. This is somewhat surprising in view of the simplicity of the model. Additional refinements should be made which would justify utilization at r values higher than those used in the calculations, except in the case of argon at 500° C. and xenon at 500° and 600° C. in LiF-BeF$_2$. For example, in the case of the smaller and less polarizable gases such as helium and neon, the actual hole radius may indeed be larger than the atomic radius due to thermal motion. As the polarizability of the rare gas atoms increases, in the order He, Ne, Ar, Xe, an ion-induced dipole interaction would cause an increasing trend in the ratio $K_{c_{\text{exptl}}}/K_{c_{\text{calcd}}}$ in this same order. The last columns in Tables II and III illustrate this point.

The cause of the comparatively large negative values of the entropy of solution of the noble gases in the LiF-BeF$_2$ mixture is not well defined. Additional experimental measurements in systems containing BeF$_2$ are needed before an attempt is made to formulate explanations as to the cause of the observed magnitude of ΔS°. As other mixtures containing BeF$_2$ are studied, the contribution of the presence of BeF$_2$ to ΔS° may become clearer.

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NOMENCLATURE

A = surface area of 1 mole of holes, sq. cm.
C = concentration, moles/cc.
ΔH = enthalpy of solution, cal./(mole)
ΔS = entropy of solution, cal./(deg.) (mole)
K = Henry's law constant, (moles gas)/(cc. melt) (atm.)
K_c = ratio of gas concentration in solution to that in gas phase, dimensionless. $K_c = K(RT)$
r = radius of gas atom, Angstrom units
t = temperature, ° C.
T = temperature, ° K.
γ = surface tension of liquid, ergs/sq. cm.
ρ = density of molten salt, g./cc.

Table III. Conparison of Calculated and Observed Values of Henry's Law Constants

Gas	Temp., ° C.	K_c[a]		$\frac{K_{c\ \text{Exptl.}}}{K_{c\ \text{Calcd.}}}$
		Exptl.	Calcd.[b]	
In LiF-BeF$_2$(64–36 Mole %)				
He	500	4.75×10^{-3}	3.50×10^{-2}	0.14
	600	8.27×10^{-3}	5.92×10^{-2}	0.14
	700	11.92×10^{-3}	8.97×10^{-2}	0.13
	800	17.15×10^{-3}	12.58×10^{-2}	0.14
Ne	500	1.96×10^{-3}	5.54×10^{-3}	0.35
	600	3.32×10^{-3}	12.5×10^{-3}	0.27
	700	5.43×10^{-3}	23.8×10^{-3}	0.23
	800	7.93×10^{-3}	40.2×10^{-3}	0.20
Ar	500	3.42×10^{-4}	2.49×10^{-4}	1.4
	600	7.02×10^{-4}	9.10×10^{-4}	0.77
	700	13.5×10^{-4}	25.7×10^{-4}	0.53
	800	23.4×10^{-4}	58.8×10^{-4}	0.40
Xe	500	0.58×10^{-4}	0.23×10^{-4}	2.5
	600	1.65×10^{-4}	1.22×10^{-4}	1.4
	700	4.07×10^{-4}	4.62×10^{-4}	0.88
	800	7.57×10^{-4}	13.5×10^{-4}	0.56
In NaF-KF-LiF (11.5–42–46.5 Mole %)[d]				
He	600	8.09[c]	52.3[c,d]	0.15
	700	14.0	79.1	0.18
	800	20.3	111.0	0.18
Ne	600	3.12	10.4	0.30
	700	6.00	19.7	0.30
	800	9.84	33.1	0.30
Ar	600	0.645	0.673	0.96
	700	1.43	1.88	0.76
	800	2.99	4.32	0.69
Xe	600	. . .	0.082	. . .
	700	. . .	0.310	. . .
	800	. . .	0.913	. . .

[a] $K_c = C_d/C_g$. [b] Surface tension of LiF-BeF$_2$ is: γ (ergs/sq. cm.) = $235.5 - 0.09t$ (° C.). [c] $K_c \times 10^3$. [d] Surface tension of NaF-KF-LiF is: γ (ergs/sq. cm.) = $237.0 - 7.88 \times 10^{-2}\, t$ (° C.).

Subscripts

d = dissolved
g = gas

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