added to the S–$SOCl_2$ solution previously prepared from the well-dried S. The immediate precipitation of S was observed where the H_2O droplets contacted the $SOCl_2$.

Thus, neither hydrolysis product causes S to precipitate from $SOCl_2$ solution, whereas H_2O itself apparently does have this effect. With this in mind, the results of the water addition experiment described above (section E) are immediately explained. Because the water was combined with a portion of $SOCl_2$ before it was added to the hot sulfur solution, what contacted the sulfur solution was primarily a solution of HCl and SO_2 in $SOCl_2$. Hence, the sulfur solubility was relatively unaffected.

Thus, while we have gained some understanding of how water and the products of the reaction between water and $SOCl_2$ affect the sulfur solubility, we have not been able to explain the scatter in the S solubility measurements themselves (since the experiments were performed with carefully dried chemicals and glassware). Nevertheless, that the averaged experimental results are reliable is certainly suggested by the good agreement between the accepted value of the S_8 heat of fusion and the values from the least-squares data analyses.

Glossary

ΔH_{fus}	heat of fusion, cal/gram formula weight
ΔH_{sol}	heat of solution, cal/mol
R	ideal gas constant, cal/(deg mol)
T	absolute temperature, K
T_0	melting point, K
x	mole fraction
α	proportionality constant

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Enthalpy of Solution of 32% Nitrogen Solutions at 25 °C

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Measurements were made of the enthalpy of solutions at 25 °C of 50.36% ammonium nitrate solution in urea solutions. Measurements also were made of the enthalpies of dilution to near infinite dilution of urea–ammonium nitrate solutions. The results were combined with published values of the enthalpies of solution of ammonium nitrate and urea, respectively, in water to determine the enthalpy of producing certain fertilizer solutions from the compounds.

The amount of energy required to avoid freezing during the preparation of 32% nitrogen solution from urea, ammonium nitrate, and water is important in the design of boilers for the process. No data are available for the enthalpy change involved.

The integral enthalpy of solution over the concentration range 0–9.7% nitrogen was determined by the scheme

$$NH_4NO_3 + xH_2O = NH_4NO_3{\cdot}xH_2O \qquad (1)$$

$$CO(NH_2)_2 + yH_2O = CO(NH_2)_2{\cdot}yH_2O \qquad (2)$$

$$NH_4NO_3{\cdot}xH_2O + a[CO(NH_2)_2{\cdot}yH_2O] = NH_4NO_3{\cdot}aCO(NH_2)_2{\cdot}(x + ay)H_2O \qquad (3)$$

$$(1) + a(2) + (3) = (4)$$

$$NH_4NO_3 + aCO(NH_2)_2 + (x + ay)H_2O = NH_4NO_3{\cdot}aCO(NH_2)_2{\cdot}(x + ay)H_2O \qquad (4)$$

where a is the mole ratio of $CO(NH_2)_2$ to NH_4NO_3 in the 32% nitrogen solution.

Table I. Solutions Used in the Determination of Enthalpy of Solution of Ammonium Nitrate Solutions in Urea Solutions

		solution compn, %	
solution	% N	$CO(NH_2)_2$	NH_4NO_3
AN	17.62		50.36
U5	2.36	5.06	
U10	4.74	10.16	
U15	7.02	15.05	

One ammonium nitrate solution and three urea solutions were prepared by dissolving the reagent-grade compounds in distilled water. The chemical analyses[2,3] and the percentages of ammonium nitrate and urea calculated from the analyses are listed in Table I.

The enthalpy of reaction 1, ΔH_1 (4220 cal), was determined by substracting the enthalpy of formation of NH_4NO_3(c) from the enthalpy of formation of 50.36% NH_4NO_3 ($NH_4NO_3{\cdot}4.380H_2O$).[5] The enthalpy of reaction 2, ΔH_2, for each urea solution was determined from the data of Egan and Luff.[1]

The ammonium nitrate solution was added to each urea solution in successive increments in the solution calorimeter and the differential enthalpy of solution, $d(\Delta H)/dm_s$, was determined in calories per mole at the average molality, m_s, of $NH_4NO_3{\cdot}4.380H_2O$ for each measurement.

The solution calorimeter and the method of measurement have been described[4] with the exception that the Wenner potentiometer and Aryton shunt were replaced by a Hewlett-Packard Model 3490A multimeter that measured the voltage drop across the calorimeter heater directly. The defined calorie was taken as 4.184 absolute J; and corrections were made for the

Table II. Observed Differential Enthalpies of Solution of $NH_4NO_3 \cdot 4.380H_2O$ in Urea Solutions at 25 °C

wt soln, g	$NH_4NO_3 \cdot 4.380H_2O$ added, g	m_s, av molality $NH_4NO_3 \cdot 4.380H_2O$	$d\Delta H/dm_s$, cal/mol
	Solvent = 5.06% Urea		
860.2276	20.912 16	0.075 56	1688
864.3836	20.903 26	0.229 94	1621
867.8107	20.227 17	0.384 84	1538
871.6013	22.794 47	0.549 82	1456
875.2427	23.724 77	0.731 97	1370
	Solvent = 10.16% Urea		
871.9454	21.985 72	0.078 33	1440
875.9889	21.681 53	0.237 49	1380
879.2134	22.017 21	0.400 03	1308
882.9999	21.464 92	0.565 18	1236
886.7188	23.287 05	0.738 47	1169
890.2392	23.674 53	0.924 24	1096
893.5970	22.896 00	1.112 68	1029
896.8775	21.632 63	1.388 42	
900.3297	22.679 53	1.483 95	914
903.3421	23.888 97	1.684 63	859
	Solvent = 15.05% Urea		
883.9395	21.233 96	0.074 67	1216
887.2908	21.810 34	0.299 36	1178
890.3382	23.380 34	0.395 05	1111
893.9785	21.716 82	0.564 14	1050
897.1552	23.316 89	0.736 42	991
900.6070	22.700 80	0.916 37	935
903.5854	21.750 15	1.094 01	881
906.5367	22.109 54	1.272 94	831
909.6591	23.068 88	1.461 06	782
912.7045	24.446 17	1.663 12	734
915.6770	22.277 37	1.866 53	692
918.5028	22.124 94	2.064 03	650
920.6951	21.958 70	2.264 30	612

Table III. Coefficients and Standard Deviations of Equations for the Differential Enthalpy of Solution of $NH_4NO_3 \cdot 4.380H_2O$ in Urea Solutions at 25 °C

	urea content of solvents, %		
coefficients	5.06	10.16	15.05
A	+1716	+1471	+1243
B	−326.8	−365.4	−303.2
C	−483.9	−159.7	−109.4
D	+38.88	+160.7	+97.50
E		−38.78	−19.66
std dev	3	2	4

heat leak, for vaporization of water into the vapor space above the liquid in the calorimeter, and for the energy of bulb breaking.

The weights of the initial solutions, the weights of ammonium nitrate solution added, the average molalities of $NH_4NO_3 \cdot 4.380H_2O$, and the observed differential enthalpies of solution for each urea solution are shown in Table II.

An equation of the form

$$d(\Delta H)/dm_s = A + Bm_s + Cm_s^2 + Dm_s^3 + Em_s^4 \quad (5)$$

was fitted to the observed values for each urea solution by the method of least squares. Integrating these equations from $m_s = 0$ to m_s and dividing by m_s gives equations of the form (Table III)

$$H = A + Bm_s/2 + Cm_s^2/3 + Dm_s^3/4 + Em_s^4/5 \quad (6)$$

Table IV. Solutions Used for Enthalpy of Dilution Measurements[a]

	compn, %		solution compn, %	
soln	total N	urea N	NH_4NO_3	$CO(NH_2)_2$
UAN-20	30.57	16.52	40.15	35.42
	grams		solution compn, %	
soln	UAN-20	H_2O	NH_4NO_3	$CO(NH_2)_2$
UAN-5	115.28	87.50	22.83	20.14
UAN-10	163.28	42.00	31.94	28.17
UAN-15	184.16	16.54	36.84	32.50

[a] a for all solutions = 1.1758.

Table V. Integral Enthalpy of Solutions of NH_4NO_3 + $1.1758CO(NH)_2$ in Water at 25 °C

	urea content of starting solutions, %		
	5.06	10.16	15.05
x	4.380	4.380	4.380
ΔH_1, cal	4220	4220	4220
y	62.548	29.477	18.817
ΔH_2, cal	3586	3516	3451
a	1.1758	1.1758	1.1758
$m_s \Bumpeq a$	0.7165	1.4388	2.1313
$(x + ay)$	77.924	39.039	26.505
ΔH_3, cal	1518	1184	909
ΔH_4, cal	9954	9538	9187
$m_t \Bumpeq m_s$	0.7123	1.4219	2.0943

Table VI. Enthalpy of Dilution and Integral Enthalpy of Solution of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ Solutions at 25 °C

solution, g	H_2O, g	final m_t	ΔH_D, cal/mol	ΔH_F, cal/mol	ΔH_I, cal/mol
starting soln, UAN-20			m_t = 20.532		
22.54149	848.8512	0.13234	3962	10329	6367
23.98397	849.0234	0.14073	3954	10323	6369
22.87070	849.2027	0.13421	3959	10328	6368
22.33336	849.0805	0.13109	3965	10330	6364
				av	6367 ± 2
starting soln, UAN-15			m_t = 15.013		
21.59870	848.9815	0.11618	3645	10340	6695
21.31013	848.9794	0.11464	3645	10341	6696
21.13629	848.9423	0.11372	3646	10341	6695
23.14370	848.9844	0.12443	3640	10334	6694
				av	6695 ± 0
starting soln, UAN-10			m_t = 10.002		
20.03760	849.1640	0.09327	3188	10355	7167
22.70026	848.6530	0.10560	3174	10347	7173
22.86702	848.8762	0.10634	3179	10346	7168
21.54494	848.9523	0.10024	3183	10351	7167
				av	7169 ± 2
starting soln, UAN-5			m_t = 4.999		
20.63416	848.8632	0.06838	2330	10372	8042
20.74020	849.0436	0.06871	2328	10372	8044
19.72306	849.0524	0.06539	2330	10374	8044
19.91961	848.8158	0.06605	2336	10374	8038
				av	8042 ± 2

In order to establish the value of a in reaction 3 and to prepare solutions for the measurement of enthalpies of dilution described later, a solution similar to the 32% nitrogen solution was prepared from reagent-grade urea and ammonium nitrate and distilled water. The concentration of $CO(NH_2)_2$ and NH_4NO_3 in the solution and the value for a were determined by chemical analysis.[3] Portions of this solution were diluted with distilled water to prepare three other solutions to be used in the enthalpy of dilution measurements. All four solutions are described in Table IV.

The enthalpy of reaction 3, ΔH_3, is the integral enthalpy of solution of $NH_4NO_3 \cdot 4.380H_2O$ in the urea solution at the concentration where the mole ratio of $CO(NH_2)_2$ to NH_4NO_3 is equal to a. Combining ΔH_1, ΔH_2, and ΔH_3 in the manner shown gives the enthalpy of reaction 4, ΔH_4, the integral enthalpy of solution of NH_4NO_3 plus $aCO(NH_2)_2$ in water to form the solution described on the right-hand side of reaction 4. If $NH_4NO_3 \cdot$

Table VII. Enthalpy of Solution of $NH_4 \cdot 1.1758CO(NH_2)_2$[a] in Water at 25 °C

% N	molality of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, m_t (eq 8)	ΔH, cal/g
2	0.3452	67.29
4	0.7283	65.82
6	1.1558	64.25
8	1.6360	62.60
10	2.1793	60.85
12	2.7990	59.00
14	3.5123	57.08
16	4.3423	55.08
18	5.3202	53.05
20	6.4893	51.02
22	7.9117	49.08
24	9.6798	47.33
26	11.9372	45.91
28	14.9193	44.79
30	19.0422	43.18
32	25.1151	36.18

[a] $NH_4NO_3 \cdot 1.1758CO(NH_2)_2 = 53.13\%$ NH_4NO_3 and 46.87% $CO(NH_2)_2$.

$aCO(NH_2)_2$ is considered as the solute and water as the solvent, the solution can be described in molality $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, m_t, since $a = 1.1758$. The determinations of the integral enthalpy of solution for the three values of m_t are described in Table V.

The integral enthalpies of solution for the solutions listed in Table IV were calculated using eq 7 where ΔH_I is the integral

$$\Delta H_I = \Delta H_F - \Delta H_D \qquad (7)$$

enthalpy of solution of the initial solution, ΔH_F is the integral enthalpy of solution of the final solution, and ΔH_D is the enthalpy of dilution. A weighed amount of the solution was diluted with a weighed amount of water in the solution calorimeter and ΔH_D in cal/mol of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ was measured. The enthalpy, ΔH_F, for each measurement was calculated from an equation of ΔH_4 as a function of m_t over the concentration range covered by the enthalpy of solution measurements listed in Table V. The observed enthalpies of dilution and the integral enthalpies of solution calculated from them are listed in Table VI.

The values of m_t and the average values of ΔH_I from Table VI were combined with the values for m_t and ΔH_4 from Table V, and eq 8, where ΔH is the integral enthalpy of solution in

$$\Delta H = 10.35 - 0.6205m_t + 0.03782m_t^2 - 0.0008313m_t^3 \qquad (8)$$

kcal/mol of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, was fitted to the observed values by the "least-squares" method with a standard deviation of 0.06 kcal/mol.

Table VII lists the enthalpies of solution of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ in calories per gram to form solutions of various nitrogen concentrations. They were determined by solving eq 8 for values of m_t corresponding to the nitrogen concentrations and dividing by 150.657 12, the gram formula weight of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$.

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Volume Changes on Mixing 1,4-Dioxane with Cyclopentane, Pentane, and 2-Methylbutane

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Measurements are reported of the excess volumes for 1,4-dioxane + *n*-pentane at 25 °C and for 1,4-dioxane + cyclopentane and 1,4-dioxane + 2-methylbutane at 20 °C. The excess volume V_m^E is positive and nearly symmetric in mole fraction for the cyclopentane mixture but changes from positive to negative with increasing mole fraction of dioxane in the other two systems. Similar variations in V_m^E with degree of branching have been observed in mixtures of C_6-alkanes with 1,4-dioxane, nitroethane, and 1-chloropentane.

Measurements at 40 °C of the excess volumes, V_m^E, for binary liquid mixtures of nitroethane with hexane isomers and with cyclohexane (*1*, *2*) show a striking dependence on the number of methyl groups in the hexane. For the mixture with cyclohexane, V_m^E is positive and nearly symmetric in mole fraction. As the number of methyl groups in the hexane is increased, the excess volume becomes increasingly smaller and skewed, eventually changing from positive to negative with increasing mole fraction of nitroethane in the 2-methylpentane system. The excess volume for the 2,2-dimethylbutane mixture changes from positive to negative at about 0.2 mol fraction nitroethane.

Similar trends have been observed in mixtures of hexanes with 1,4-dioxane (*2*) and with 1-chloropentane (*3*), strengthening the supposition that they reflect the properties of the hexane. Mixtures of hexanes with hexadecane also display a trend toward increasingly negative volume changes (*4*), but there is no accompanying change in the shape of the V_m^E vs. mole fraction curve. A recent study of cyclohexane + hexadecane (*5*) demonstrates that the V_m^E is positive.

No completely satisfactory explanation of these trends has been put forward. In an effort to gain more insight into the problem, we are investigating volume changes in related systems. We report here results for binary mixtures of 1,4-dioxane with cyclopentane, *n*-pentane, and 2-methylbutane.

Experimental Section

Volume Change Measurements. Details of the measurements, which were made with a continuous dilution dilatometer,

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