Thermodynamic Properties of Polar Substances

Enthalpy of Hydrocarbon-Alcohol Systems

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THE INDUSTRIAL interest in petroleum compounds has generated large amounts of data for both pure components and mixtures of hydrocarbons. These data and the general similarity in molecular structure of the components have made it possible to develop reasonably precise methods for predicting thermodynamic properties of hydrocarbons over a wide range of conditions. When chemically dissimilar mixtures are encountered, much larger deviations from ideal behavior are observed. Furthermore, data for these systems are meager. As a result, adequate prediction methods have not appeared for such systems. This article presents experimental enthalpy data for the binaries and pure components in the systems benzene-ethyl alcohol and *n*-pentane–ethyl alcohol.

Enthalpy data for nonpolar-polar mixtures over a range of temperatures and pressures are generally not available. McCracken and Smith (*4*) have reported measurements on binary mixtures of benzene-methanol over extended ranges of temperature and pressure. They proposed a correlating procedure based upon association of the methanol. Data for one composition of a ternary system, *n*-hexane–benzene-methanol, were also reported.

SCOPE OF EXPERIMENTAL INVESTIGATION

Enthalpies were measured for pure ethyl alcohol, benzene, and *n*-pentane, and binary mixtures containing 25, 50, and 75 mole % ethyl alcohol in benzene and *n*-pentane. These data covered a temperature range of 250° to 500° F. at pressures from 50 to 1700 p.s.i.a. Additional information was obtained in the critical region.

Heat of mixing data of the liquids were used in order to place all mixture enthalpies on the same basis: pure liquid components at 77° F. and their individual vapor pressures. The heats of mixing of Schnaible and others (*7*) were used for the benzene-ethyl alcohol system. Measured values for the *n*-pentane–ethyl alcohol system were not available, but were estimated to be 7.8, 9.4, and 8.7 B.t.u. per pound of mixture at 25° C. for the 75, 50, and 25 mole % ethyl alcohol mixtures, respectively. The experimental results covered both liquid and vapor regions.

EXPERIMENTAL

The experimental method was the same as used by McCracken and Smith (*4*). This involves the measurement of the energy transferred from the mixture flowing through a double-jacket calorimeter to boiling Freon 11. The enthalpy change between the states at the inlet and the outlet to the calorimeter could be calculated from the weight of Freon evaporated and its latent heat of vaporization. The mixture leaving the calorimeter was always cooled to a temperature within 2° F. of the atmospheric boiling point of the Freon, 74° F. The exit stream was liquid at this temperature for all of the mixtures investigated.

Detailed drawings and description of the apparatus have been presented (*4*).

RESULTS

The steady-state energy balance across the calorimeter, neglecting kinetic and potential energy changes, gives the following expression for the change in enthalpy of the fluid stream:

$$\Delta H_c = \frac{-L_f W_f}{W_m} \tag{1}$$

Correction must be made to the ΔH_c values obtained from Equation 1 to refer the enthalpies to the desired standard state. There are three corrections.

Entrance and Exit Temperature Deviations. A correction was necessary to allow for the deviation of the actual inlet temperature from the desired isothermal temperatures. This correction, Δh_1, was generally less than 2 B.t.u. per pound. Small corrections, Δh_2, were also made to account for the outlet temperatures which were different from the desired 77° F. reference temperature.

Effect of Pressure on Liquid Enthalpy at 77° F. An approximate correlation of the isothermal effect of pressure on the enthalpy of liquids has been prepared by Hougen and Watson (*2*). Calculations for the pure liquids used in this work indicated that at 77° F., the change in enthalpy was less than the assignable experimental error for pressures from the vapor pressure up to the critical value. On this basis, the enthalpy of the liquids at 77° F. and elevated pressure were assumed to be the same as for the liquid in its standard state.

Heats of Mixing. The pure component enthalpies at 77° F. and their vapor pressures are related to the enthalpy of the exit stream through the heat of mixing, ΔH_m^0, by the expression:

$$H_m^0 = \Delta H_m^0 + \sum_i x_i H_i^0 \tag{2}$$

The superscript zero refers to the datum state. The mixture enthalpy, H_m^0, is equal to the mixture enthalpy from the calorimeter because the summation of $x_i H_i^0$ is zero by the definition of the standard states.

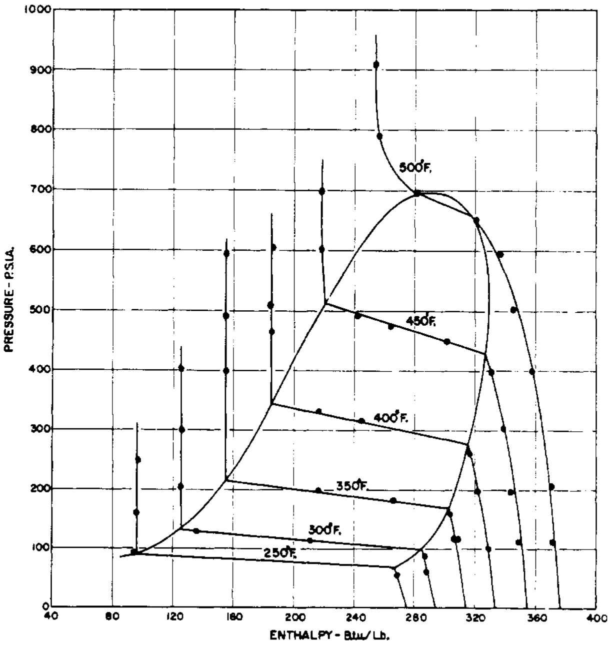

Figure 1. Pressure-enthalpy diagram
Mixture: 75 mole % benzene, 25 mole % ethyl alcohol
Datum: H = O, pure liquid components at 77° F.

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When the three corrections are applied to Equation 1, the enthalpy in any state, H_1, referred to the pure liquid at the standard state of 77° F. is given by the expression:

$$H_1 = \frac{L_f W_f}{W_m} + \Delta h_1 + \Delta h_2 + \Delta H_m^0 \qquad (3)$$

Operation of the equipment was most convenient when the inlet temperature was held constant and the pressure varied as each sample was taken . Each series of runs at constant temperature establishes an isotherm on a pressure-enthalpy diagram. The intersection of the three distinct curves obtained below the critical temperature represented points on the phase envelope. A series of isotherms would then define the phase envelope for the mixture. The data are illustrated by the points shown in Figures 1 and 2 on pressure-enthalpy coordinates. [Figures for other compositions of the binary systems and for the pure components are included in reference (*9*).] The curves represent smoothed data obtained by cross-plotting the pressure-enthalpy data on temperature-enthalpy and pressure-temperature diagrams and adjusting the curves until agreement was obtained among the three plots. Additional data were taken in the critical region at constant pressure at close temperature intervals. These data were used to define more accurately the critical region on the temperature-enthalpy diagrams, and they are not shown in Figures 1 and 2.

PRECISION OF RESULTS

Enthalpy data for the mixtures are not available for comparison with the data. Values have been published for pure benzene, *n*-pentane, and ethyl alcohol. Organick and Studhalter (*5*) presented a pressure-enthalpy diagram for benzene based on available heat capacity, latent heat of vaporization, and *P-V-T* data. The standard deviation between the experimental data for benzene obtained in this study and these literature values was 1.8 B.t.u. per pound. with a mean difference of 0.2 B.t.u. per pound. A similar comparison of the experimental *n*-pentane data with the pressure-enthalpy data presented by Edmister (*1*) yielded a standard deviation of 2.8 B.t.u. per pound. As the possible errors in the values presented in these references are at least as large as the quoted deviations, the results for benzene and *n*-pentane verify the accuracy of the experimental procedure. Information on ethyl alcohol presented by Smith and Reid (*8*) and more recently by Papini and Cuomo (*6*) agreed satisfactorily with the experimental data in the low pressure regions. At high pressures, wide deviations were observed. Inaccuracies introduced in computing enthalpies from approximate volumetric data for ethyl alcohol probably contributed a major portion of this

Table I. Thermodynamic Properties of Saturated and of Superheated Benzene

(Datum: H = O, liquid benzene at 77° F.)

Saturated Benzene

Pressure P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./Lb. Liquid	Enthalpy, B.t.u./Lb. Vapor
100	320	110	253
200	388	146	274
300	436	172	288
400	472	193	297
500	502	217	302
600	527	240	303
700	550	267	295
716	553	283	283

Superheated Benzene

Temperature, ° F.

Enthalpy, B.t.u./Lb.

	250	300	350	400	450	500	550
0	240	256	276	295	316	338	361
100	74	99	266	289	310	331	356
200	74	99	125	280	303	328	351
300	74	99	125	152	295	322	345
400	...	...	125	152	181	314	338
500	...	...	...	152	181	219	330
600	...	...	...	...	181	217	317
700	...	...	...	...	...	215	[a]
800	...	...	...	...	...	213	260
900	...	...	...	...	...	212	253
1000	...	...	...	...	...	211	248

[a] Fluid saturated at this condition.

Table II. Thermodynamic Properties of Saturated and of Superheated *n*-Pentane

(Datum: H = O, liquid *n*-pentane at 77° F.)

Saturated *n*-Pentane

Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u/Lb. Liquid	Enthalpy, B.t.u/Lb. Vapor
100	223	91	216
200	287	130	236
300	330	165	254
400	363	194	260
450	378	211	251
485	387	236	236

Superheated *n*-Pentane

Temperature, ° F.

Enthalpy, B.t.u./Lb.

	250	300	350	400	450	500
0	235	262	291	322	349	380
100	227	254	285	315	345	376
200	105	244	278	309	339	372
300	105	140	268	301	333	367
400	105	140	180	289	325	361
500	105	140	178	269	316	354
600	...	140	178	233	303	347
700	...	...	178	222	287	339
800	...	...	...	220	275	330
900	...	...	...	...	266	321
1000	...	...	...	...	261	314
1100	...	...	...	...	257	307

Table III. Thermodynamic Properties of Saturated and of Superheated Ethyl Alcohol

(Datum: H = O, liquid ethyl alcohol at 77° F.)

Saturated Ethyl Alcohol

Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./Lb. Liquid	Enthalpy, B.t.u./Lb. Vapor
100	278	148	453
200	327	188	461
300	360	221	464
400	387	249	466
500	409	276	467
600	428	298	464
700	443	317	455
800	456	331	441
900	467	361	413
927	470	388	388

Superheated Ethyl Alcohol

Temperature, ° F.

Enthalpy, B.t.u./Lb.

	250	300	350	400	450	500
0	463	487	510	534	560	587
100	123	469	496	524	552	581
200	123	166	479	512	543	573
300	123	166	212	499	533	566
400	...	166	212	482	521	558
500	...	166	212	266	507	548
600	...	...	212	266	489	537
700	...	...	...	266	464	525
800	...	...	...	266	321	511
900	...	...	...	...	319	495
1000	...	...	...	...	318	475
1100	...	...	...	...	318	444
1200	...	...	...	...	318	411
1300	...	...	...	...	...	395
1400	...	...	...	...	...	387
1500	...	...	...	...	...	381

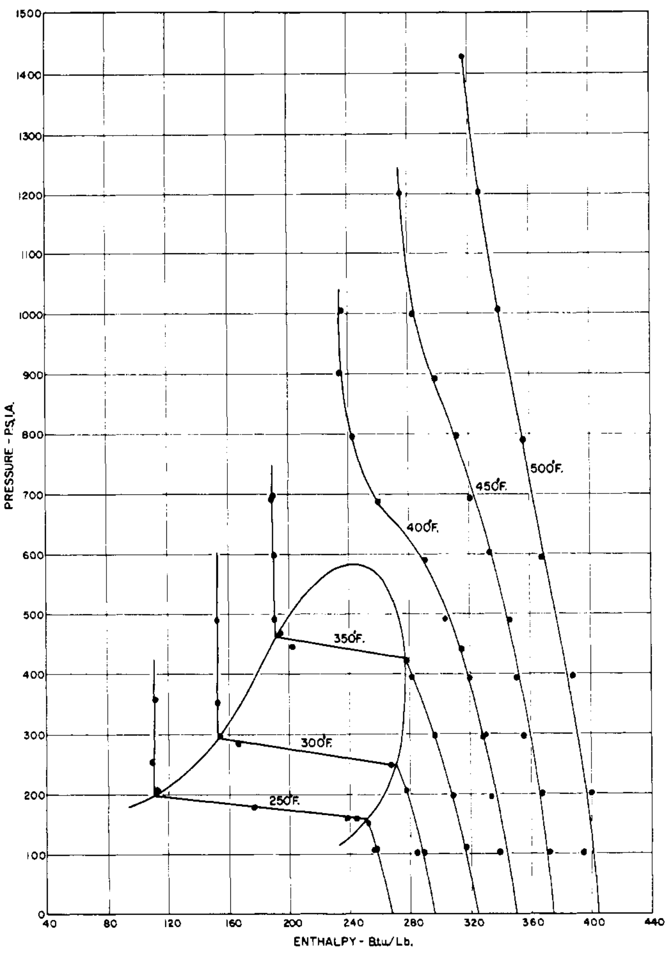

Figure 2. Pressure-enthalpy diagram

Mixture: 75 mole % *n*-pentane, 25 mole % ethyl alcohol
Datum: *H* = O, pure liquid components at 77° F.

Table IV. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 75 Mole % Benzene and 25 Mole % Ethyl Alcohol

(Datum: H = O, pure liquid components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
100	270	105	301	285
200	342	151	365	307
300	384	176	407	317
400	417	196	440	325
500	444	218	469	329
600	469	242	493	326
650	483	257	500	319
693	502	290	502	290

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	275	293	313	333	354	376
100	96	277[a]	308	329	351	373
200	96	125	209[a]	322	346	369
300	96	125	155	273[a]	340	365
400	...	125	155	185	331	358
500	...	...	155	185	238[a]	349
600	...	...	155	185	219	333
700	...	...	...	...	218	279
800	...	...	...	...	...	256
900	...	...	...	...	...	254

[a] Two phase region.

Table V. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 50 Mole % Benzene and 50 Mole % Ethyl Alcohol

(Datum: H = O, pure liquid components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
100	269	121	281	324
200	325	161	337	342
300	365	189	375	350
400	396	211	405	355
500	420	231	432	357
600	442	249	455	357
700	462	274	473	346
750	474	301	477	325
756	478	313	478	313

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	321	341	362	383	406	427
100	109	333	357	378	401	424
200	109	143	350	371	395	419
300	109	143	178	362	387	414
400	109	143	178	270[a]	378	408
500	...	143	178	214	368	400
600	...	...	...	214	322[a]	391
700	...	...	...	214	256	379
800	...	...	...	...	255	361
900	...	...	...	...	254	321
1000	...	...	...	...	...	297
1100	...	...	...	...	...	292
1200	...	...	...	...	...	291

[a] Two phase region.

Table VI. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 25 Mole % Benzene and 75 Mole % Ethyl Alcohol

(Datum: H = O, pure liquid components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
100	273	134	278	377
200	321	175	327	391
300	355	202	362	400
400	381	224	390	405
500	403	244	414	407
600	424	262	435	407
700	443	279	453	404
800	460	300	469	394
900	475	334	479	361
906	479	348	479	348

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	382	403	425	448	472	496
100	96	390	416	440	466	492
200	96	157	405	433	460	487
300	96	157	199	424	452	482
400	...	157	199	413	444	475
500	...	...	199	241	433	468
600	...	...	...	241	419	458
700	...	...	...	241	368[a]	447
800	...	...	...	241	286	434
900	...	...	...	...	284	417
1000	...	...	...	...	284	394
1100	...	...	...	...	284	360
1200	...	...	...	...	...	344
1300	...	...	...	...	...	335
1400	...	...	...	...	...	332
1500	...	...	...	...	...	330

[a] Two phase region.

discrepancy. Hence, the experimental data presented in this paper are believed to be the most reliable information for ethyl alcohol.

The maximum assignable experimental errors were divided into the following sources:

Source	Maximum Error, B.t.u./Pound
Temperature measurement	0.3
Pressure measurement	0.2
Freon collecting and weighing	0.2-0.5
Sample collecting and weighing	0.2-1.5
Total	0.9-2.5

The high error in the sample collecting and weighing occured when runs were made on materials with relatively high enthalpies. A small error in weighing these samples corresponds to a large error in the measured enthalpy. For most operating conditions, the maximum total assignable error should be nearer the lower limit, about 1 B.t.u. per pound.

TABULATED DATA

Figures 1 and 2 illustrate the type of smoothed *P-H* diagram obtained for each pure component and mixture studied. Tables of values were prepared by reading points on the smoothed curves. These results are shown in Tables I to IX. The tables extend up to the critical point, and the critical temperature and pressure for each composition are given.

Generalized correlations are available (*2*, *3*) for predicting the effect of pressure on the enthalpy of gases. The Hougen and Watson method (*2*) was originally developed for hydrocarbons and later extended (*3*) to all substances. The data in Tables I to IX can be used to test these correlations by comparing the enthalpy deviation from the ideal gas, or zero pressure, values. As would be expected, the agreement is reasonably good for benzene, average deviations being 1.4 B.t.u. per pound for correlation (*2*) and 0.65 B.t.u. per pound for correlation (*3*). Similarly, the correlations predict

Table VII. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 75 Mole % *n*-Pentane and 25 Mole % Ethyl Alcohol

(Datum: H = O, pure liquids components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
200	253	131	276	282
300	302	173	318	294
400	334	196	345	295
500	359	219	365	291
550	370	236	373	283
582	378	262	378	262

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	287	314	342	369	393	423
100	277	305	336	362	389	420
200	129	297	326	356	384	415
300	129	171	314	346	378	409
400	129	171	300	337	371	402
500	...	171	209	324	362	395
600	...	...	208	305	353	387
700	...	...	208	275	341	380
800	...	...	...	260	328	373
900	...	...	...	254	313	365
1000	...	...	...	252	302	358
1100	...	...	...	...	296	352
1200	...	...	...	...	293	346
1300	...	...	...	...	...	341

Table VIII. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 50 Mole % *n*-Pentane and 50 Mole % Ethyl Alcohol

(Datum: H = O, pure liquid components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
200	265	147	284	328
300	296	174	317	336
400	323	200	342	341
500	347	228	364	341
600	372	262	381	332
650	386	290	389	315
657	390	304	390	304

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	333	359	386	411	436	466
100	320	350	380	407	433	463
200	137	338	372	401	428	459
300	137	209[a]	362	394	423	454
400	137	179	346	385	418	449
500	137	179	251[a]	372	410	442
600	...	...	229	353	401	435
700	...	...	227	318	389	428
800	...	...	...	282	373	419
900	...	...	...	274	356	410
1000	...	...	...	270	342	398
1100	...	...	...	...	331	388
1200	...	...	...	...	324	380
1300	...	...	...	...	320	374
1400	...	...	...	...	316	369

[a] Two phase region.

Table IX. Thermodynamic Properties of a Saturated and of a Superheated Mixture Containing 25 Mole % *n*-Pentane and 75 Mole % Ethyl Alcohol

(Datum: H = O, pure liquid components at 77° F.)

Saturated Mixture

	Liquid		Vapor	
Pressure, P.S.I.A.	Temp., ° F.	Enthalpy, B.t.u./lb.	Temp., ° F.	Enthalpy, B.t.u./lb.
100	245	131	263	385
200	293	171	309	400
300	323	201	339	403
400	348	227	363	405
500	370	251	385	405
600	389	273	403	404
700	407	294	419	399
800	425	323	430	377
826	432	350	432	350

Superheated Mixture

	Temperature, ° F.					
	250	300	350	400	450	500
	Enthalpy, B.t.u./Lb.					
0	393	418	443	469	494	525
100	227[a]	409	436	463	489	521
200	134	279[a]	425	456	484	517
300	134	178	411	446	478	511
400	134	178	250[a]	435	471	505
500	134	178	228	421	462	499
600	...	...	228	381[a]	451	490
700	...	...	228	285	437	481
800	...	...	228	282	419	471
900	...	...	...	280	389	459
1000	...	...	...	279	358	446
1100	...	...	...	...	342	430
1200	...	...	...	...	333	414
1300	...	...	...	...	328	403
1400	...	...	...	...	324	395
1500	...	...	...	...	322	390

[a] Two phase region.

the data for *n*-pentane with an average deviation of 1.8 and 1.4 B.t.u. per pound. However, these methods are unsatisfactory for ethyl alcohol as indicated by average deviations of 10.8 B.t.u. per pound (32%) for correlation (*2*), and 10.7 B.t.u. per pound (31%) for correlation (*3*). The same correlations can be used to estimate the enthalpy deviations for the ethyl alcohol–hydrocarbon mixtures using a pseudocritical point concept. Here again, the errors are large when compared with the data of Tables I to IX. The average deviations range from 3 to 46%, depending upon the hydrocarbon content of the mixture. The conventional generalized correlations, while satisfactory for hydrocarbons, are not suitable for ethyl alcohol or its mixtures with benzene and pentane.

NOMENCLATURE

h = enthalpy correction applied to data points
H = enthalpy at any pressure, smoothed enthalpy data
L = latent heat of vaporization
T = absolute temperature
W = weight
x = mole fraction

Superscript

^{0} = datum state, 77° F.

Subscripts

c = critical property; calorimeter in Equation 1
f = formation or Freon 11
i = component in a mixture
m = mixture property or mixture
1 = inlet to the calorimeter
2 = outlet to the calorimeter or dimer

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Rare Earth and Yttrium Fluorides

Solubility Relations in Various Molten NaF-ZrF_4 and NaF-ZrF_4-UF_4 Solvents

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AS PART of an extensive study of phase relations in molten fluoride mixtures, the solubilities of cerium, lanthanum, samarium, and yttium trifluorides (LaF_3, CeF_3, SmF_3, and YF_3) in various solvent compositions were determined. Inasmuch as the series of rare earths offers distinct regularity of properties in both elemental and combined states, it was hoped that these solubility measurements might allow some interesting comparisons to be made. In addition, because the rare earth trifluorides are known to form solid solutions, and the liquidus temperatures involved in these systems are high, equilibria might be reached rapidly enough to effect a rare earth extraction by a solid solvent.

The solubilities of some rare earth fluorides, (principally those of samarium, europium, and gadolinium) are also important in designing a nuclear reactor fueled with a molten fluoride mixture containing fissionable material. These three rare earths are expected to account for significantly more than half of the nuclear poisoning by nongasous elements. Consequently, information obtained in this work was expected to be pertinent to design of a poison depletion process and to give assurance that precipitation of these fission products will not hinder the operation of a reactor.

Because the fission products formed in greater yields include several of the rare earths, rare gases, alkaline earths, and the 4*d* transition elements (particularly elements Nos. 41-46), the selection of subjects for initial study was made after considering relative importance based on fission yield and thermal neutron cross sections of the various products. This report presents some of the data obtained in this laboratory on the solubility of LaF_3, CeF_3, SmF_3, and YF_3 in a sodium, zirconium, and uranium fluoride solvent consisting of 50 mole % NaF, 46 mole % ZrF_4 and 4 mole % UF_4. Two pseudo-ternary systems, LaF_3-CeF_3-solvent and CeF_3-SmF_3-solvent have also been studied, as have various other mixtures of fission products to determine their solubility relations. Several series of experiments were carried out using NaF-ZrF_4 solvents of other compositions so that some information relating to the shape of the liquidus surface in the NaF-ZrF_4-CeF_3 system could be obtained. In addition to delineating the allowable rare earth concen-

Table I. Solubilities of CeF_3 in Solvents of Various Compositions at Three Temperatures

Solvent Composition, Mole %[a]		Molecular Wt. Used for Solvent Mixture, G./Mole	Mole % CeF_3 at		
NaF	ZrF_4		550° C.	675° C.	800° C.
42	58	114.6	3.0	8.2	10.3
50	50	104.5	2.12	3.0	4.4
53	47	100.9	1.64	2.37	3.9
59	41	93.3	0.56	0.62	1.61
63	37	88.4	0.26	0.44	1.07
80.5	19.5	66.4	...	...	4.71

[a] ±0.5 mole %.