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Introduction

Liquid ammonia in many of its reactions and properties simulates water. Next to water liquid ammonia is the best known electrolytic solvent. It dissolves a large number of salts to form, in general, conducting solutions, in which the ions are more mobile.

Ammonium salts in liquid ammonia solution act in a manner analogous to acids in water. They attack metals, react with metallic ammonium bases and oxides. The reaction is much slower than in water.

Ex. $NH_4Cl + Na = NaCl + NH_3 \; H$

The ammonium salts ionize to form the ammoniated hydrogen ion.

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     H            H
  H:N: + H⁺ = H:N : H
     H            H
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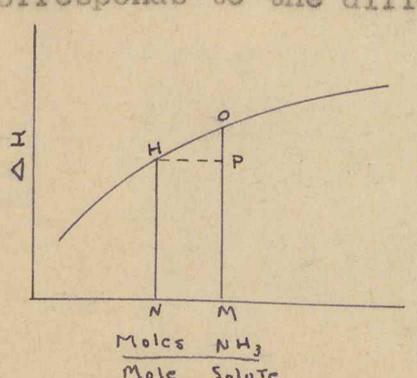
The ammoniated hydrogen ion is simular to the solvated hydrogen ion H O

Discussion of the Curves

In each case the heat evolved, in small calories, per gram mole solute is plotted against the moles of liquid ammonia per mole of solute. As the concentration decreases the curve approaches a constant value which corresponds to the differential heat solution.



The value of the ordinates NH and MO is the integral heat of solution in N and M moles of solvent. The difference between them, OP, is the integral heat of dilution corresponding to a change in concentration from N moles to M moles.

Dilution Curve. The heat of dilutes is plotted against the change in the moles of ammonia. The curves approach a constant value which is the heat of dilution. These curves were plotted to compare the heat of dilution of ammonium chloride and ammonium bromide.

Discussion

The comparison between the heats of solution of Inorganic salts in water and liquid ammonia, procedure and sample calculations can be found in the Journal of the American Chemical Society (cf. ref. 4). Sottysiak's Thesis contains the calorimeter constant, volume of pipette, and accompaning data.

Due to the installation of a new galvanometer and accracy between 1% and 2% can be claimed for the above data. The method of absorbing the evolved ammonia (simular to that used by Kraus and Prescott) still causes trouble. If a new absorbing system could be installed the accracy could be increased to less than 1%. In heats such as those obtained for lead iodide a small percentage error causes a considerable absolute error. With the present apparatus a varation of 300 calories would be within the limits of experimential error for heats of solution in lead iodide.

The values obtained for the ammonium chloride and ammonium bromide are in fair agreement with those obtained by Kraus and Ridderhof.

The rate of solution seems to be an important factor in the amount of ammonia evolved. At present there seems no way of illaminating this fault.

Note: A positive ΔH in this article denotes an exothermic heat effect. A negative ΔH an endothermic heat effect.

References.

1. The Nitrogen System of Compounds by Franklin
2. Kraus and Prescott J. Am. Chem. Soc. 56, 86, (1934)
3. Kraus and Schmidt J. Am. Chem. Soc. (1935)
4. Kraus and Ridderhof J. Am. Chem. Soc. 56, 79, (1934)
5. Sottsiak's Thesis (1934-1935)

Table 1

Data of Heats of Solution of Ammonium Bromide in Liquid Ammonia

Wt. of sample in grs.	Wt. of NH_3	Grs. NH_3 evolved by sol.	ΔT of sol.	Time in Min.	Moles of NH_3/Mole of NH_4Br.	ΔH(sol) total	ΔH(sol) Molar
.4957	24.81	.08146	.78	2.5	288.4	52.649	10405
.8101	24.66	.2311	.23		175.4	82.919	10040
1.2523	24.60	.2862	.84	1.7	112.9	121.25	9489
1.4959	24.51	.3836	.30	5.5	94.25	134.77	8825
1.8070	24.49	.4003	.81	3.0	77.99	157.91	8560
2.4423	24.36	.5348	.63	6.0	57.38	195.92	7858

The ammonium bromide was recrystallized from water twice, then dried in a desiccator. The pressure in the bulb was not more than fifteen microns.

Table 2

Data on Heats of Solution of Ammonium Chloride in Liquid Ammonia

Wt. of sample in grs.	Wt. of NH_3	Grs. NH_3 evolved by sol.	ΔT of sol.	Time in Min.	Moles of NH_3/Mole of NH_4Cl.	ΔH(sol) total	ΔH(sol) Molar
.7710	24.65	.2384	.27	2.0	103.20	92.32	6406
1.5547	24.44	.4462	.67	1.0	50.95	172.59	5939

Confer Sottsiak's Thesis for remaining points.

Table 3

Data of Heats of Solution of Lead Iodide in Liquid Ammonia

Wt. of sample in grs.	Wt. of NH_3	Grs. NH_3 evolved by sol.	ΔT of sol.	Time in Min.	Moles of NH_3/mole of PbI_2	ΔH(sol total	ΔH(sol) Molar
.7733	24.78	.1073	.33		869.1	46.06	27460
1.0755	24.73	.1621	.32	5.7	638.2	63.67	27295
2.1772	24.55	.3447	.36	3.7	305.8	124.75	26420
2.4281	24.48	.4104	.08	4.2	273.4	136.90	26025

Lead iodide had been measured. Since it had a high heat and was insoluable in water, it was decided to determine its heat. A value lower than that quoted in the reference was obtained.

The heat of solution of lead iodide represents a heat of reaction with liquid ammonia to give a colorless solution of an ammoniated lead iodide.

The lead iodide was analysed by converting to the sulfate and weighing as such. The results are given below.

Wt. of PbI_2	Wt. of $PbSO_4$	Wt. of Pb	Percent Pb
1.4559 grs.	.9138 grs.	.6244 grs.	42.94
.4988 "	.3176 "	.2170 "	43.50

The calculated percentage for lead in lead iodide is 44.93%. After washing the lead iodide twice with distilled water and drying, it was analysed again. The results were in good agreement with the theoretical percentage.

Table 4

Data on Exothermic Heats of Solution in Liquid Ammonia

Compound	Wt. of sample in grs.	Grs. NH_3 evolved by sol.	Wt. of NH_3 in grs.	ΔT of sol.	ΔH(sol) total	ΔH(sol) Molar
RbBr	.6271	none	24.89	.05	1.664	438.0
Pyridine	1.1150	none	24.89	.53	-17.64	-1250
Ethanol	2.0260	.06652	24.82	1.31	65.24	1483

Since water had been measured, it was thought adviseable to measure the heat of solution of the alcbhols. One measurement was made on ethanol as an indicator. The ethanol was dried by refluxing over anhydrous copper sulfate and distilled out of the container.

Pyridine is a cyclic ketone in the nitrogen system. It was dried and redistilled before making a measurement.

Table 5

Data on Heats of Dilution of Ammonium Chloride in Liquid Ammonia

Initial concentration 25 moles of NH_3/ mole of NH_4Cl

Δn	ΔH
0	0
40	1600
80	1885
120	2065
160	2165
200	2215
240	2225

Initial concentration 60 moles of NH_3/ mole of NH_4Cl

Δn	ΔH
0	0
40	310
80	490
120	605
160	660
200	670
240	675

The above values were read from the heat of solution curve of ammonium chloride.

Δn- change in moles of ammonia.
ΔH- change of heat of solution.

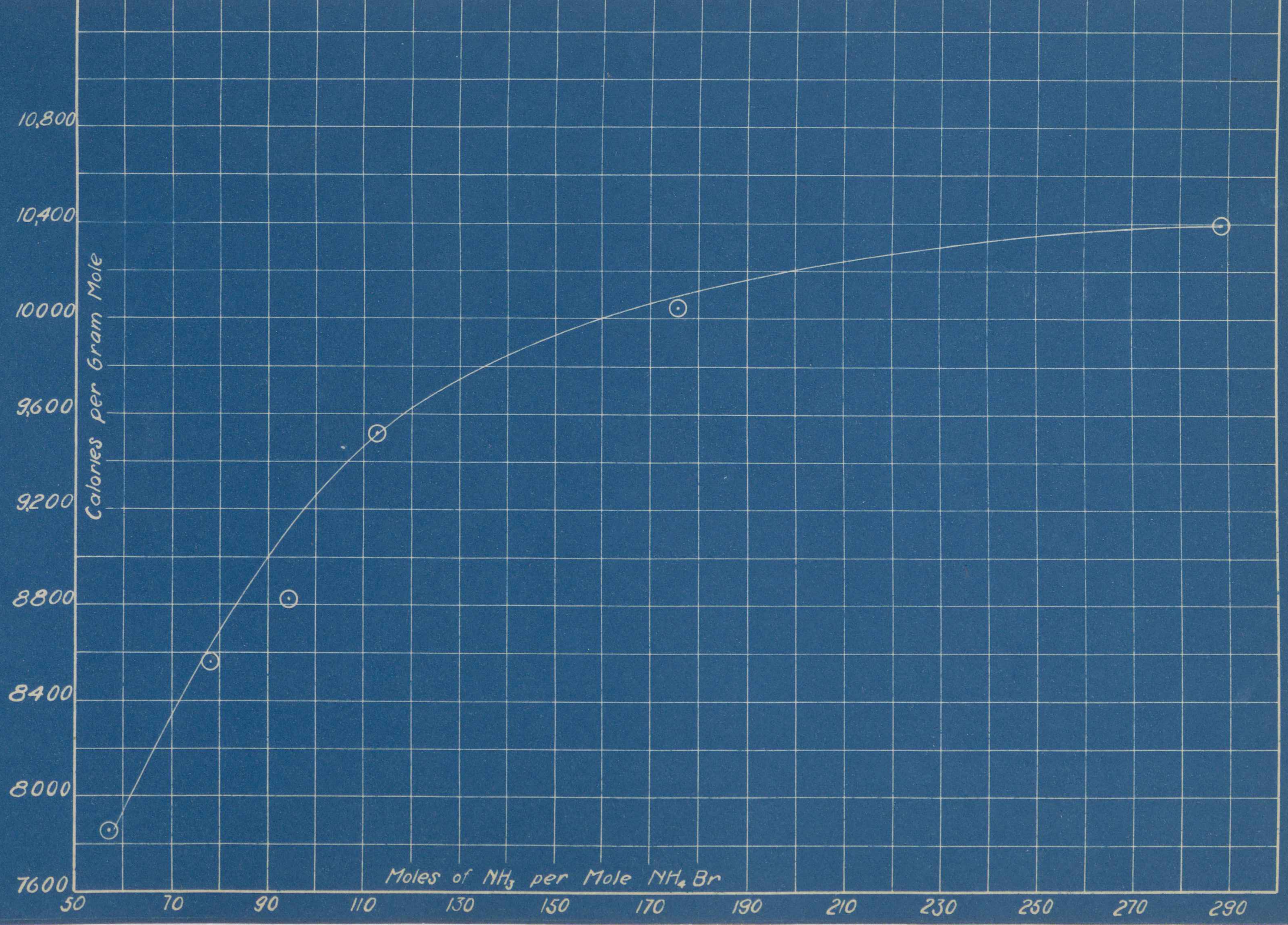
Table 6

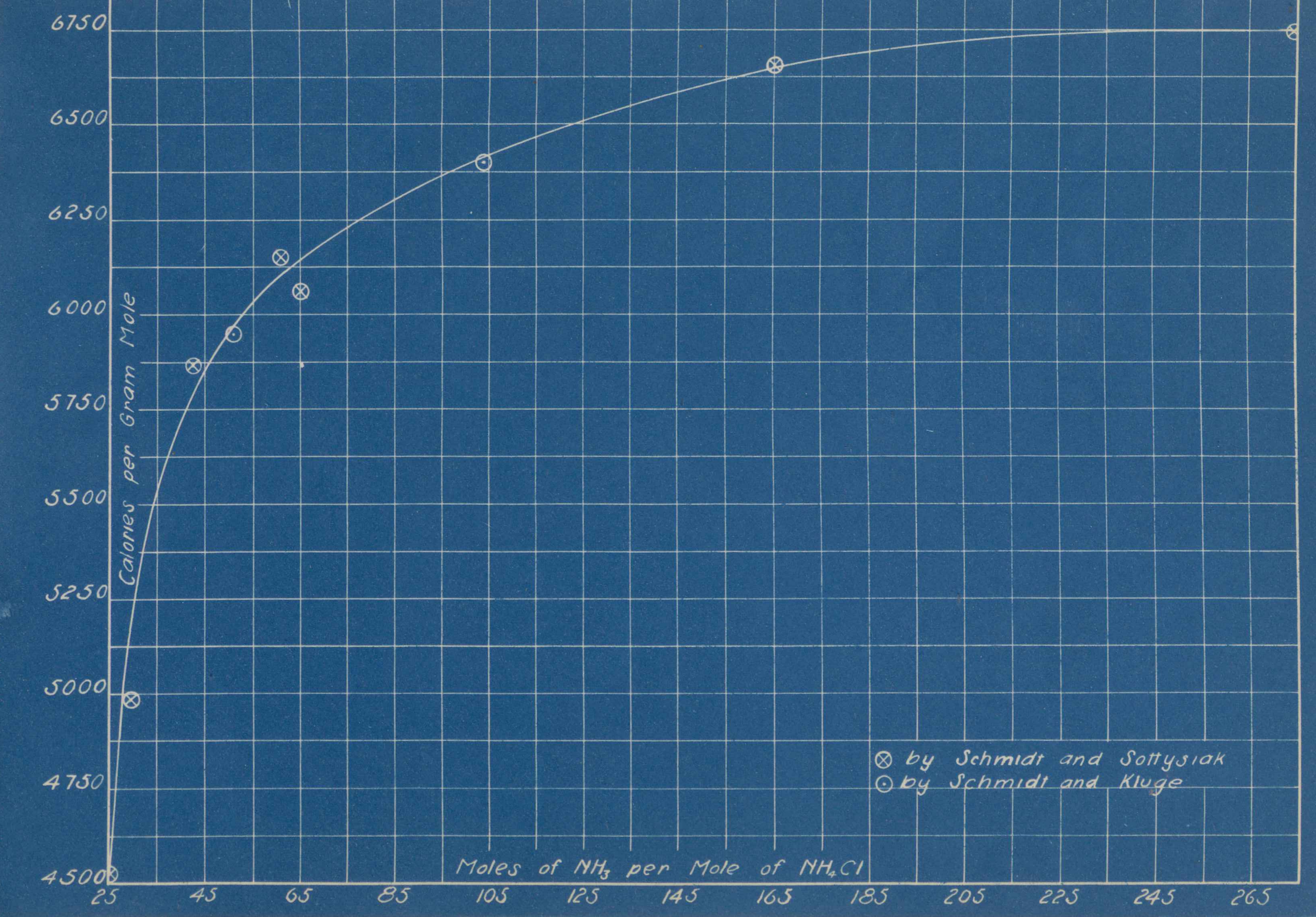
Data on Heats of Dilution of Ammonium Bromide in Liquid Ammonia

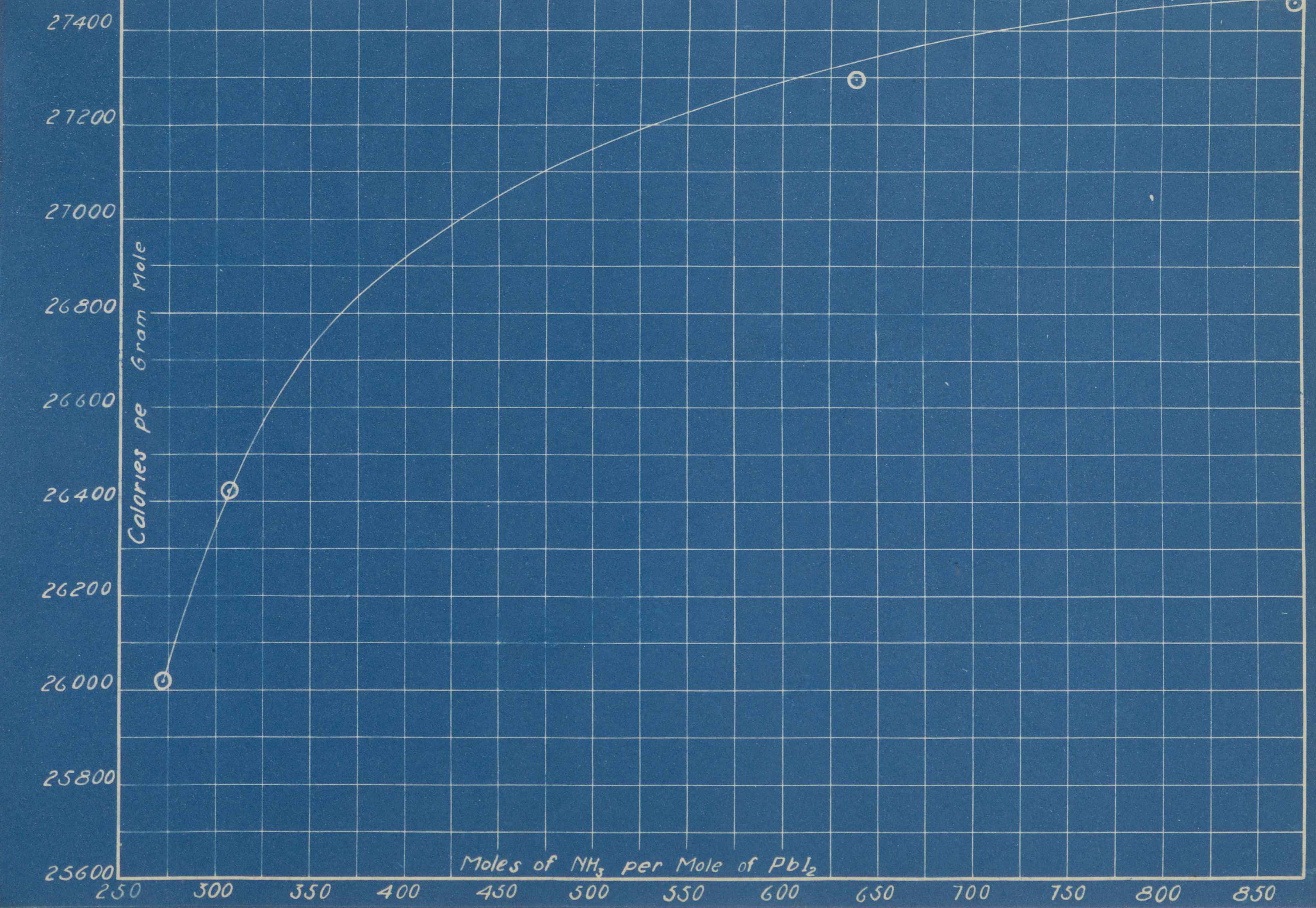
Initial Concentration 60 moles of NH_3/ mole of NH_4Br.

Δn	ΔH
0	0
40	940
80	1620
120	1990
160	2190
200	2280
240	2340

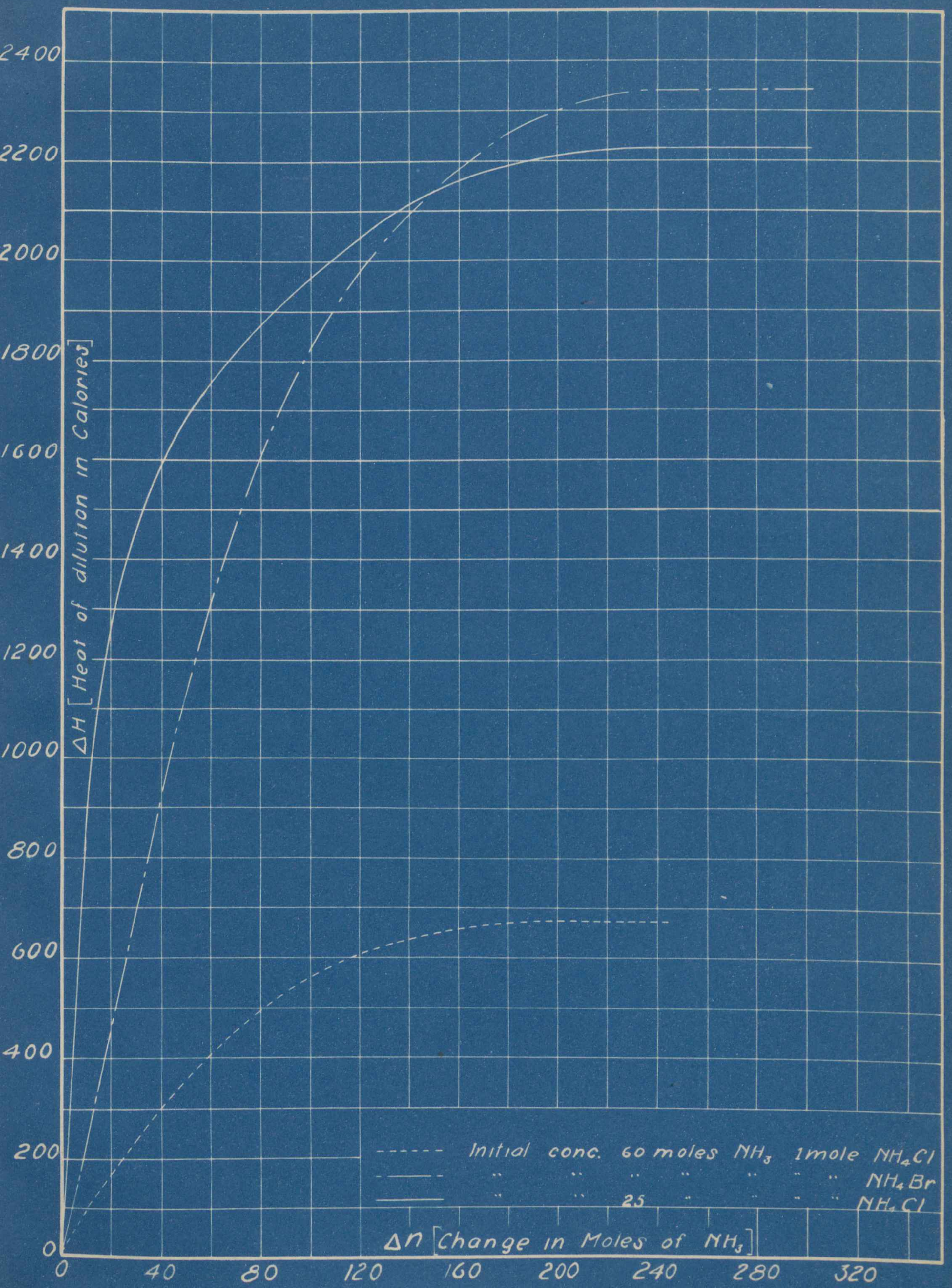
The above values were read from the heat of solution curve of ammonium bromide. Δn-and ΔH have same values as above.


10,800
10,400
10000
9,600
9,200
8800
8400
8000
7600
Calories per Gram Mole
50
70
90
110
130
150
170
190
210
230
250
270
290
Moles of NH3 per Mole NH4 Br


6750
6500
6250
6000
5750
5500
5250
5000
4750
4500
Calories per Gram Mole
25
45
65
85
105
125
145
165
185
205
225
245
265
Moles of NH3 per Mole of NH4Cl
⊗ by Schmidt and Sottysiak
⊙ by Schmidt and Kluge



Calories pe Gram Mole
27400
27200
27000
26800
26600
26400
26200
26000
25800
25600
Moles of NH_3 per Mole of PbI_2
250
300
350
400
450
500
550
600
650
700
750
800
850



2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
ΔH [Heat of dilution in Calories]
0
40
80
120
160
200
240
280
320
Δn [Change in Moles of NH_3]
Initial conc. 60 moles NH_3 1 mole NH_4Cl
" " " " " " NH_4Br
" " 25 " " " " NH_4Cl