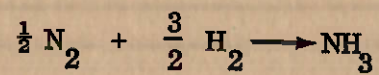


THE ENTHALPY DIAGRAM FOR THE REACTION



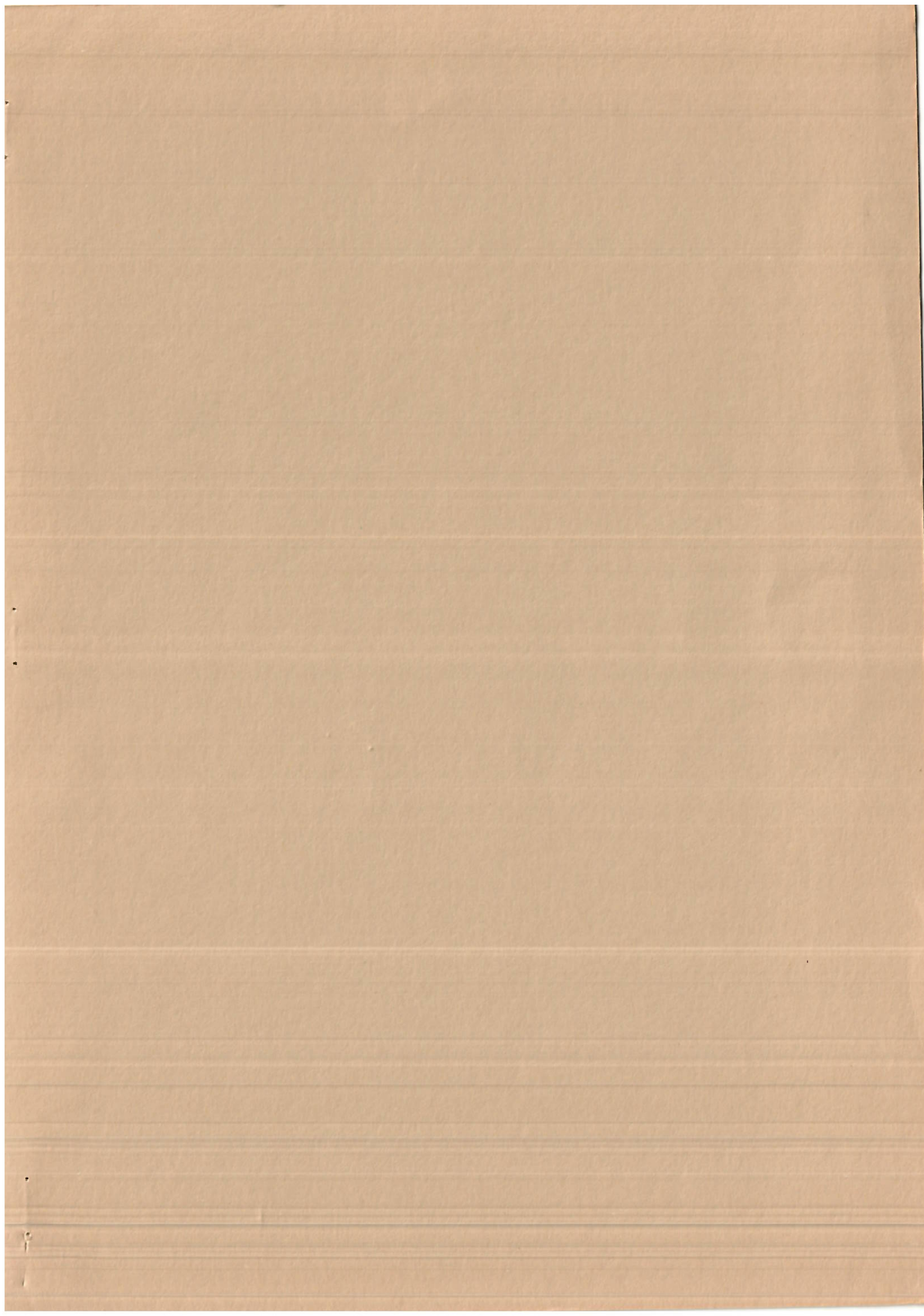
Energy Conversion Technical Report No. 9

by

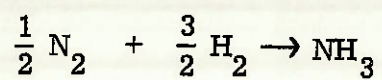
R. W. REVIE

July, 1975

Department of Engineering Physics
Research School of Physical Sciences
THE AUSTRALIAN NATIONAL UNIVERSITY
Canberra, A. C. T. Australia



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ENERGY CONVERSION TECHNICAL REPORT NO. 9

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R. W. REVIE

Engineer

Energy Conversion Group

Department of Engineering Physics

Australian National University

Canberra, Australia

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1. INTRODUCTION

The aim of this investigation was to establish the enthalpy diagram for the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$; i. e., the graph of enthalpy, H, vs temperature, T, at various pressures, P. The establishment of the enthalpy diagram is an essential part of the proposed development of a solar energy plant based on the dissociation and synthesis of ammonia. (1)

The approach to the enthalpy diagram in this report is to determine first, in Section 2, the enthalpy of ammonia using

- (a) standard thermodynamic equations at atmospheric pressure;
- (b) the pressure-enthalpy diagram for ammonia, Figure 1;² and
- (c) the graph of enthalpy correction for gases as a function of pressure, Figure 2.³

The values of ΔH for the reaction $\frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightarrow \text{NH}_3$ were then computed, in Section 3, following the approach of Gillespie and Beattie⁴ using the Beattie-Bridgeman equation of state. Finally, in Section 4, the enthalpies of the $\text{N}_2 - \text{H}_2$ mixture were evaluated from the values of H for ammonia and of ΔH for the reaction. The enthalpies of $\text{N}_2 - \text{H}_2$ were also checked, in Section 4, by independent calculation.

2. THE ENTHALPY OF AMMONIA

Pressure = 1 atm.

It is conventional in thermodynamics to regard the enthalpy of the elements to be zero in their equilibrium states at 25°C.⁵ Accordingly, the enthalpies of nitrogen and hydrogen were taken as zero at 25°C and 1 atm pressure.

The enthalpy of ammonia at 1 atm as a function of temperature was calculated using the basic thermodynamic equation

$$H_T = H_{298} + \int_{298}^T C_p dT \dots (1)$$

For ammonia,

$$C_p = 7.11 + 6.00 \times 10^{-3}T - 0.37 \times 10^{-5}T^2 \text{ cal deg}^{-1} \text{ mole}^{-1} \quad (6)$$

The enthalpies calculated in this way are shown in Table 1.

TABLE I

Enthalpy of Ammonia as a Function of Temperature
at Atmospheric Pressure

T	-H
°C	k cal/mole
0	11.21
37	10.90
87	10.46
107	10.28
127	10.09
207	9.33
300	8.39
500	6.17
600	4.97
700	3.71

ELEVATED PRESSURES

Enthalpy calculations at pressures greater than 1 atmosphere were based on:

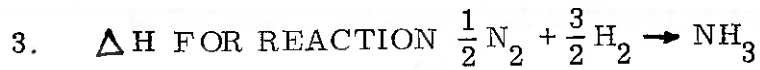
1. Pressure-enthalpy diagram for ammonia, reproduced in Figure 1. (2)

2. Graph of enthalpy correction for gases as a function of pressure reproduced in Figure 2. ⁽³⁾

Calculations based on the P-H diagram (Figure 1) were limited to temperatures below 580°K (307°C), the maximum temperature on the diagram. In using the enthalpy correction graph (Figure 2), the reduced temperature and pressure of ammonia were calculated using the values of 405.6°K and 111.5 atm for the critical temperature and pressure, ⁽⁷⁾ respectively. The enthalpy values determined are presented in Table II.

TABLE II
Enthalpy of Ammonia as a Function of Temperature at
Elevated Pressures

$T^{\circ}\text{C}$	$-H, \text{ k cal/mole}$										
	0	37	87	107	127	207	300	500	600	700	
P, atm											
1	11.21	10.90	10.46	10.28	10.09	9.33	8.39	6.17	4.97	3.71	
100	16.52	15.76	14.75	14.27	12.10	10.04	8.90	6.45	5.17	3.95	
300	16.44	15.72	14.79	14.39	13.97	11.81	9.70	6.85	5.53	4.11	
600	16.27	15.63	14.77	14.41	14.04	12.43	10.49	7.29	5.89	4.31	
1,000	16.05	15.48	14.68	14.36	14.00	12.52	10.69	7.49	6.05	4.47	



From the definition of enthalpy, (8)

$$dH = TdS + VdP,$$

where S and V refer to enthalpy and volume, respectively

$$\therefore \frac{\partial H}{\partial P}_T = V + T \frac{\partial S}{\partial P}_T$$

From the Maxwell relation, (9)

$$\frac{\partial S}{\partial P}_T = - \frac{\partial V}{\partial T}_P,$$

$$\frac{\partial H}{\partial P}_T = V - T \frac{\partial V}{\partial T}_P$$

Integrating for n moles of gas at constant temperature,

$$H = n \int_0^P \left[V - T \frac{\partial V}{\partial T}_P \right] dP + nh \quad \dots \quad (2)$$

where h is the molar enthalpy as $P \rightarrow 0$.

From the definition of C_P , the heat capacity at constant pressure,

$$h = \int_{T_0}^T C_P dT + h_0$$

where h_0 is the molar enthalpy at temperature T_0 .

As $P \rightarrow 0$, any gas behaves as an ideal gas.

$$\therefore C_P - C_V = R, \quad (10)$$

where C_V is the heat capacity at constant volume and R is the gas constant.

$$\therefore h = \int_{T_0}^T (C_V + R)dT + h_0$$

$$h = \int_{T_0}^T C_V dT + RT - RT_0 + h_0$$

$$h = \int_{T_0}^T C_V dT + RT + u_0 \dots \dots \dots (3)$$

where u_0 is the molar internal energy at temperature T_0 .

The Beattie-Bridgeman equation of state⁽¹¹⁾ explicit in molar volume, V_m , is

$$V_m = \frac{RT}{P} + \frac{\beta}{RT} + \frac{\gamma P}{(RT)^2} + \frac{\delta P^2}{(RT)^3} \dots \dots (4)$$

$$\text{where } \beta = RTB_0 - A_0 - \frac{Rc}{T^2}$$

$$\gamma = -RTB_0 b + A_0 a - \frac{Rc B_0}{T^2}$$

$$\text{and } \delta = \frac{RB_0 bc}{T^2}$$

A_0 , B_0 , a , b , and c are constants characteristic of each gas, and the values for hydrogen, nitrogen, and ammonia are tabulated in Table III⁽⁴⁾. Differentiating eqn (4) and multiplying by T ,

$$T \frac{\partial V_m}{\partial T} / P = \frac{RT}{P} + \frac{A_0}{RT} + \frac{3c}{T^3} + \dots \dots \dots$$

$$V_m - T \frac{\partial V_m}{\partial T} \Big|_P = B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3} + \dots \quad (5)$$

TABLE III

Values of the equation of state constants (4)

Units: atmospheres, litres mole⁻¹, °K

$$R = 0.08206$$

Gas	A ₀	a	B ₀	b	c	Normal volume
Hydrogen	0.1975	-0.00506	0.02096	-0.04359	0.0504 x 10 ⁴	22.4252
Nitrogen	1.3445	0.02617	0.05046	-0.00691	4.20 x 10 ⁴	22.4015
Ammonia	2.3930	0.17031	0.03415	0.19112	476.87 x 10 ⁴	22.1022

Combining equations (2) and (5),

$$H = \int_0^P n \left[B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3} + \dots \right] dP + nh$$

$$H = \left[B_0 - \frac{2A_0}{RT} - \frac{4c}{T^3} \right] nP + nh \quad (6)$$

where terms containing powers of P higher than one are omitted.

The heat absorbed at constant pressure by a chemical reaction is

$$\Delta H = \sum (\nu_i H_i),$$

where ν_i is the number of moles of substance i in the stoichiometric

equation for the chemical reaction, and is negative if the substance disappears in the reaction. Following the approach of Gillespie and Beattie⁴, using eqn (6),

$$\Delta H = \left[\sum (\nu_i B_{oi}) - 2 \sum \left(\nu_i \frac{A_{oi}}{RT} \right) - 4 \sum \left(\frac{\nu_i C_i}{T^3} \right) \right] P + \sum \nu_i h_i$$

A solution for $\sum (\nu_i h_i)$ is found as follows:

$$C_{V_i} = A_i + B_i T + C_i T^2,$$

where A_i , B_i and C_i are constants for each gas, tabulated in Table IV⁽⁴⁾. From eqn (3),

$$h_i = \int_{T_0}^T (A_i + B_i T + C_i T^2) dT + RT + u_{oi}$$

TABLE IV

Values of the specific heat constants⁽⁴⁾

Units: cal mole⁻¹ °K⁻¹

R = 1.986847

Gas	A	10 ³ B	10 ⁶ C
Hydrogen	4.66	0.70	0.00
Nitrogen	4.82	0.33	0.05
Ammonia	6.04	0.71	5.10

$$h_i = (A_i + R)T + \frac{B_i T^2}{2} + \frac{C_i T^3}{3} - A_i T_0 - \frac{B_i T_0^2}{2} - \frac{C_i T_0^3}{3} + u_{o_i}$$

$$\begin{aligned} \sum (\nu_i h_i) &= \left[\sum (\nu_i A_i) + \sum (\nu_i) R \right] T + \frac{\sum (\nu_i B_i)}{2} T^2 + \frac{\sum (\nu_i C_i)}{3} T^3 - \sum (\nu_i A_i) T_0 \\ &\quad - \frac{\sum (\nu_i B_i)}{2} T_0^2 - \frac{\sum (\nu_i C_i)}{3} T_0^3 + \sum \nu_i u_{o_i} \end{aligned}$$

Following Gillespie and Beattie,⁴

$$\text{let } I = \frac{M}{R} \left[\sum (\nu_i A_i) T_0 + \frac{\sum (\nu_i B_i)}{2} T_0^2 + \frac{\sum (\nu_i C_i)}{3} T_0^3 - \sum (\nu_i u_{o_i}) \right]$$

where $M = 0.43429 \dots$ is the modulus of the common logarithms.

$$\therefore \sum (\nu_i h_i) = \left[\sum (\nu_i A_i) + \sum (\nu_i) R \right] T + \frac{\sum (\nu_i B_i)}{2} T^2 + \frac{\sum (\nu_i C_i)}{3} T^3 - \frac{R}{M} I$$

Using the constants in Tables III⁽⁴⁾ and IV⁽⁴⁾ and the value of

$$\sum (\nu_i u_{o_i}) = -10059.2 \text{ calories, as determined by Gillespie and Beattie}^{(4)},$$

the equation for ΔH is

$$\begin{aligned} \Delta H &= - \left[0.54526 + \frac{840.609}{T} + \frac{459.734 \times 10^6}{T^3} \right] P - 5.34685T \\ &\quad - 0.2525 \times 10^{-3} T^2 + 1.69167 \times 10^{-6} T^3 - 9157.09 \end{aligned}$$

where ΔH is the heat absorbed in the formation of one mole of ammonia from its elements in calories, P is in atmospheres, and T is in degrees Kelvin. Values calculated from this equation are presented in Table V.

The data in Table V are in reasonable agreement with those in Figure 3⁽¹²⁾ which shows the $-\Delta H$ of the synthesis reaction as functions

of temperature and pressure, as obtained from theoretical and experimental studies. These values consider 100% conversion into NH_3 , and do not include any heat of mixing of NH_3 with the N_2 and H_2 . The corrected values are appreciably different only for pressures above 300 atm; (13, 14) for example, at 300 atm and with a 17.6% conversion, the enthalpy at 500°C decreases by 4%, but under the same conditions at 1000 atm, it decreases by 11%.

TABLE V

Heat evolved ($-\Delta H$) in the formation of one mole of ammonia from its elements at several temperatures and pressures

$T^\circ\text{C}$	$-\Delta H$, calories				
	0	300	500	600	700
P, atm					
1	10,630	11,990	12,660	12,890	13,040
100		12,430	12,920	13,110	13,230
300		13,320	13,450	13,550	13,610
600		14,660	14,240	14,210	14,190
1000		16,440	15,290	15,090	14,950

4. ENTHALPY OF $(\frac{1}{2}N_2 + \frac{3}{2}H_2)$

The enthalpy of $\frac{1}{2}N_2 + \frac{3}{2}H_2$ as a function of temperature and pressure was calculated from the enthalpy of NH_3 and ΔH for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$; i. e.,

$$H(\frac{1}{2}N_2 + \frac{3}{2}H_2) = H(NH_3) - \Delta H. \text{ The data so obtained}$$

are presented in Table VI. As a check on the data obtained by this method, independent data for a 3 : 1 H_2 - N_2 mixture were also obtained in the following ways:

- (a) at 1 atm, by calculation using equation (1). For nitrogen $C_p = 6.66 + 1.02 \times 10^{-3} T \text{ cal deg}^{-1} \text{ mole}^{-1}$ (15) and for hydrogen

$$C_p = 6.52 + 0.78 \times 10^{-3} T + 0.12 \times 10^{-5} T^2 \text{ cal deg}^{-1} \text{ mole}^{-1} \text{ (16)}$$

- (b) at elevated pressures, from the generalized charts for departures of enthalpy from ideal gas behaviour, which are based on the theorem of corresponding states. (17) The critical pressure and temperature of N_2 were 33.5 atm and 126.1° K, respectively. (7) For H_2 , the critical constants are 12.8 atm and 33.3° K (7), but, as discussed by Comings, (18) in using the theorem of corresponding states, the critical constants of low-molecular-weight gases, such as hydrogen, must be increased by 8 in the calculation of reduced temperature and pressure; i. e., in these cases,

$$T_R = \frac{T}{T_c + 8} \text{ and } P_R = \frac{P}{P_c + 8}$$

where the subscripts R and C indicate reduced and critical, respectively.

Data obtained in these ways are presented in Table VII

TABLE VI

Enthalpy of $(\frac{1}{2}N_2 + \frac{3}{2}H_2)$ calculated from $H(NH_3)$
and $\Delta H(\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3)$

T ^o C	H($\frac{1}{2}N_2 + \frac{3}{2}H_2$), k cal				
	0	300	500	600	700
P, atm					
1	-0.58	3.65	6.49	7.92	9.33
100		3.53	6.47	7.94	9.28
300		3.62	6.60	8.02	9.50
600		4.17	6.95	8.32	9.88
1,000		5.75	7.80	9.04	10.48

Comparison of the data in Tables VI and VII shows reasonable agreement between the data obtained by the different methods.

The data plotted in the enthalpy diagram, Fig. 4, are those obtained by difference plus the data in Table VII at 0 and 150^oC and pressures greater than 1 atm.

TABLE VII

Enthalpy of $(\frac{1}{2}N_2 + \frac{3}{2}H_2)$ calculated independently
of $H(NH_3)$ and ΔH

$H(\frac{1}{2}N_2 + \frac{3}{2}H_2)$, k cal						
$T^{\circ}C$	0	150	300	500	600	700
P, atm						
1	-0.35	1.74	3.84	6.69	8.15	9.61
100	-0.36		3.87			
300	-0.41	1.72 *	3.84			
600	-0.43	1.71	3.83			
1,000	-0.23 *	2.08 *				

* This value obtained from Figure 2.

5. RECOMMENDATIONS FOR FUTURE WORK

- (a) The heat of mixing of NH_3 , H_2 , and N_2 , should be considered for accurate enthalpy calculations including both incomplete dissociation and synthesis of ammonia.

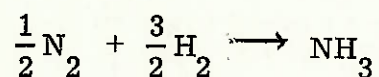
(b) An investigation of the accuracy of the theorem of corresponding states for the $\text{NH}_3 - \text{N}_2 - \text{H}_2$ system needs to be carried out.

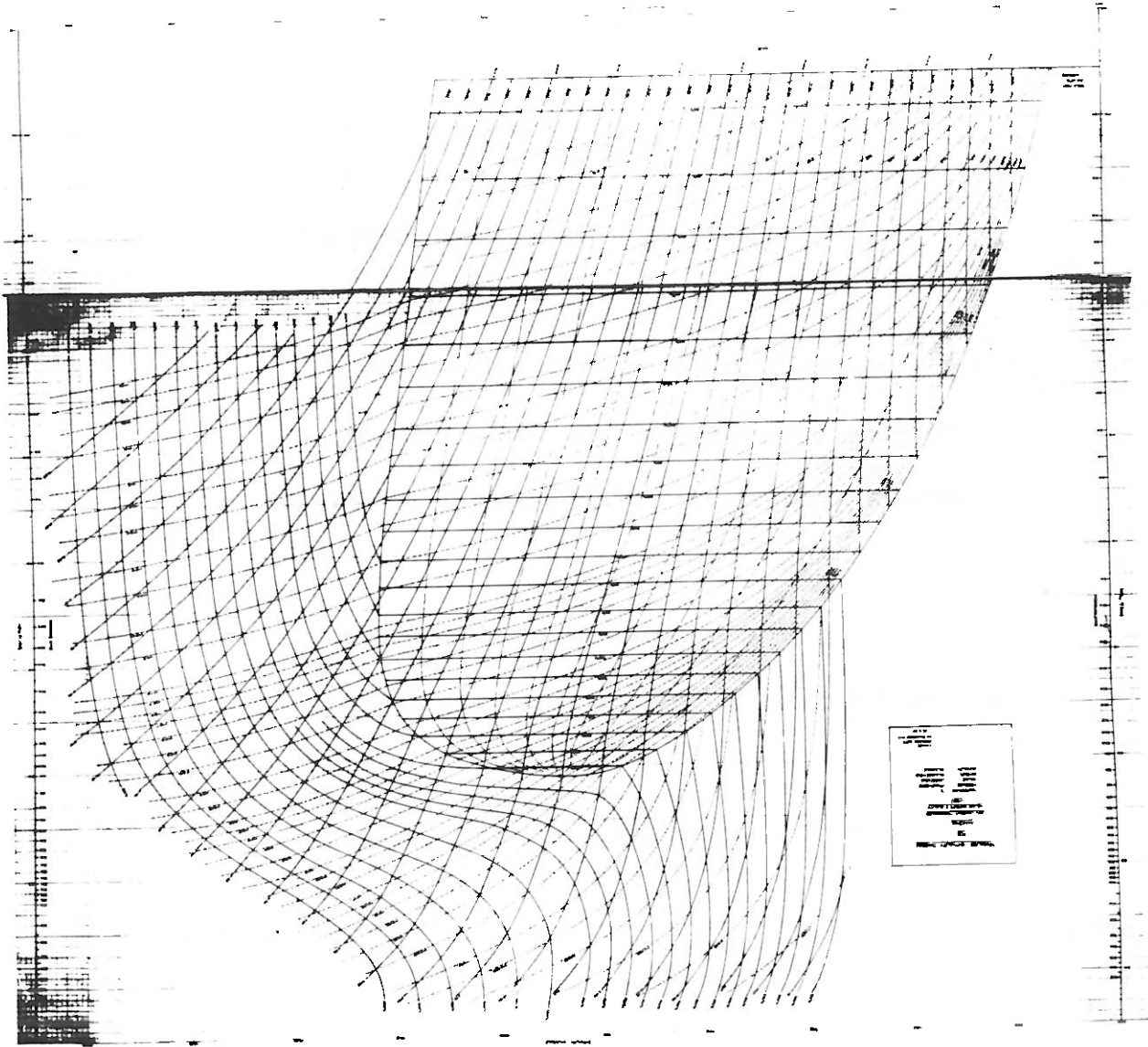
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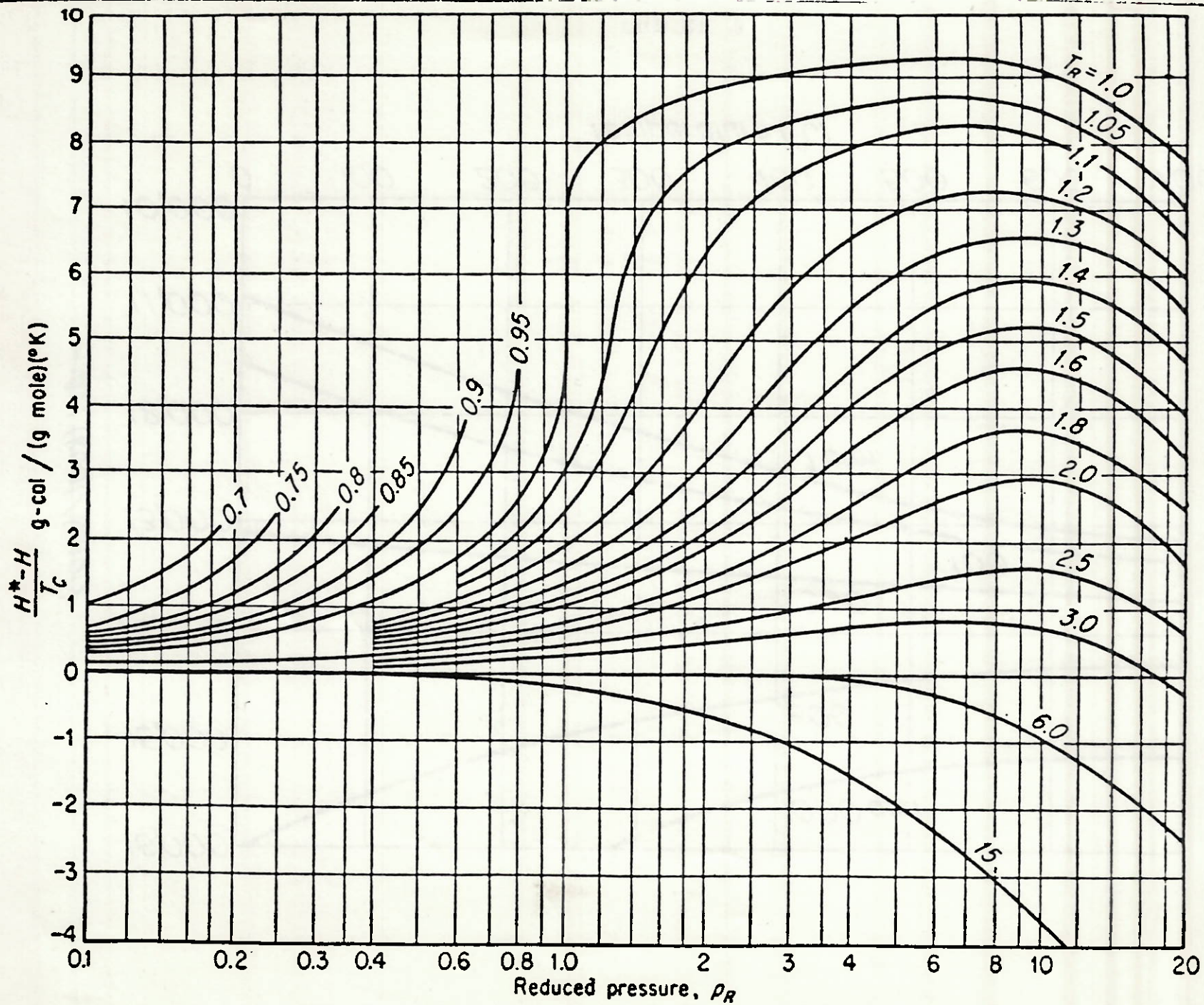


FIGURE 2.

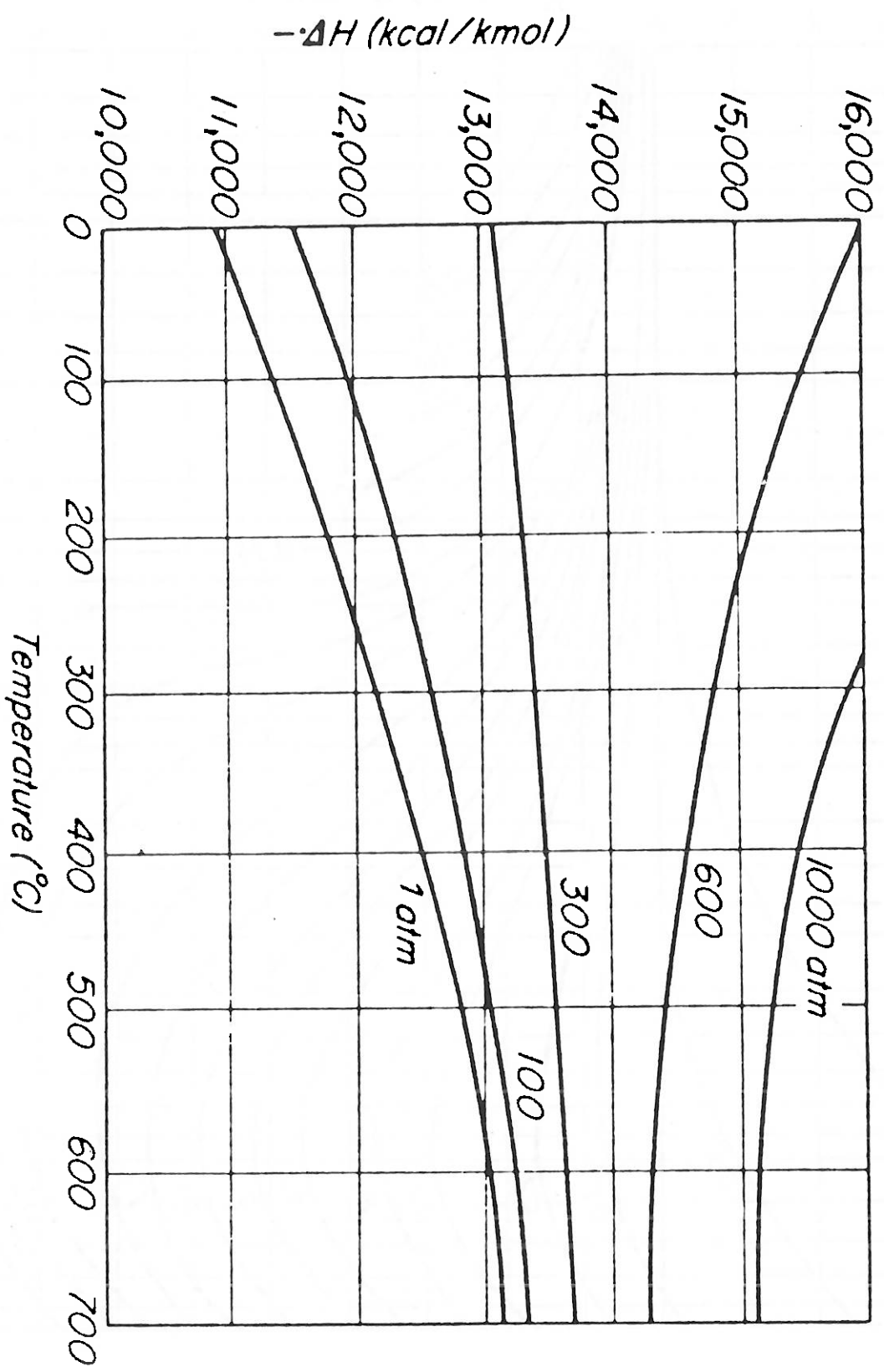


FIGURE 3.

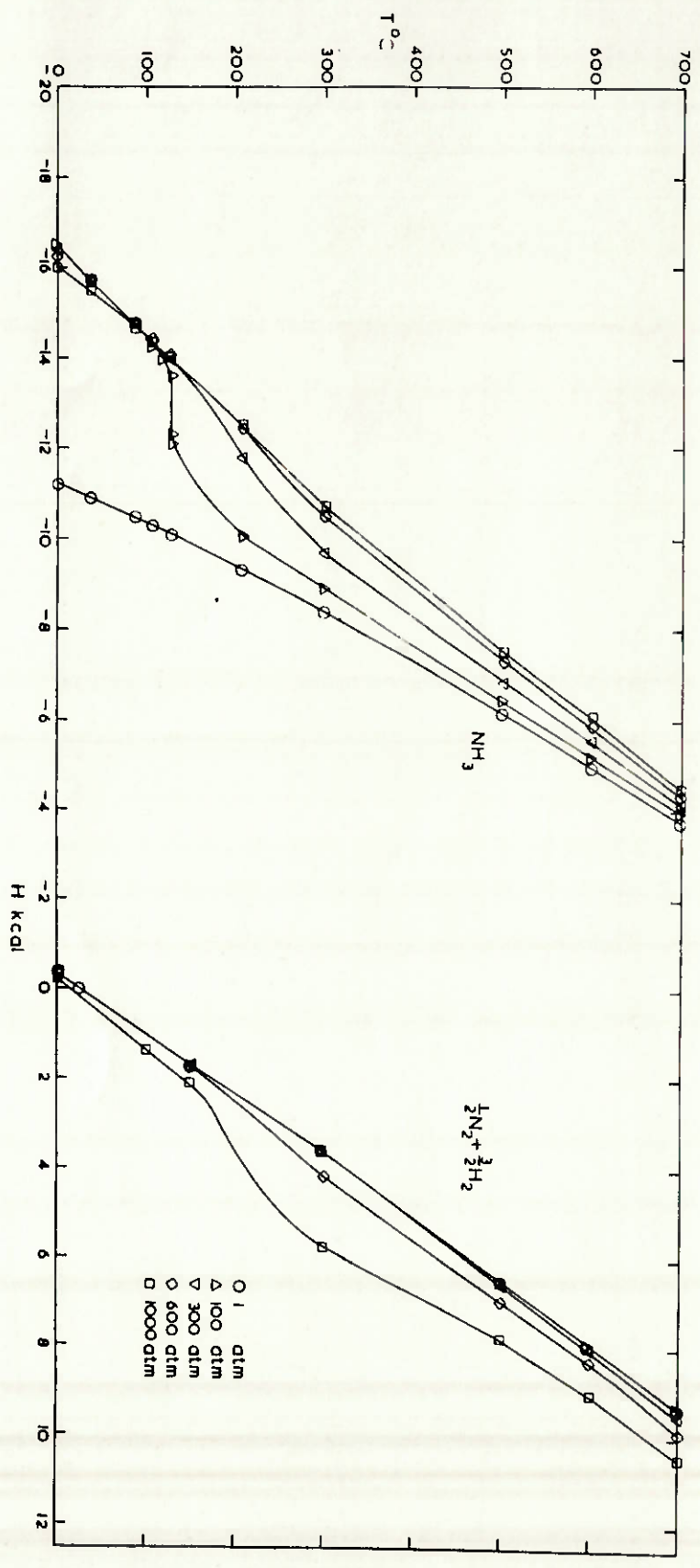


FIGURE 4

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