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B12

TK 39.377

KFKI-71-68

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ISOTOPE EFFECT ON VAPOUR PRESSURE, V.  
EFFECT OF DEUTERIUM SUBSTITUTION  
ON THE VAPOUR PRESSURE OF METHYLAMINE,  
ETHYLAMINE AND PROPYLAMINE

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CENTRAL  
RESEARCH  
INSTITUTE FOR  
PHYSICS



BUDAPEST



2017



SUMMARY

The differences between the vapour pressures of ethylamine, propylamine and their derivatives generated at the same group were determined over a wide range of temperatures. Using the experimental data and the virial equations for amine vapours, the separation factor ( $\alpha$ ) was evaluated for each pair of isotopic compounds and fitted by the method of least squares to Stielson's equation:  $\ln \alpha = A/T^2 - B/T$ .

# ISOTOPE EFFECT ON VAPOUR PRESSURE, V. EFFECT OF DEUTERIUM SUBSTITUTION ON THE VAPOUR PRESSURE OF METHYLAMINE, ETHYLAMINE AND PROPYLAMINE

ABSTRACT

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Summary of the paper, including the authors' names and affiliation, and a brief description of the work. The text is mirrored from the reverse side of the page.

KIVONAT

Az izotópjelölés hatására a metilamin, etilamin és propilamin és a hozzájuk tartozó derivátumok gőznyomásának különbségeit meghatároztuk egy széles hőmérséklet-tartományban. A kísérleti adatokból és az aminok virial egyenleteiből a szétválasztási tényezőt ( $\alpha$ ) az egyes izotópjelölésű vegyületek párosára értékeltük ki, és a Stielson-egyenlettel:  $\ln \alpha = A/T^2 - B/T$  legkisebb négyzetes módszerrel illesztettük.



## SUMMARY

The differences between the vapour pressures of methylamine, ethylamine, propylamine and their derivatives deuterated at the amine group were determined over a wide range of temperatures. Using the experimental data and the virial equations for amine vapours, the separation factor  $\alpha$  was evaluated for each pair of isotopic compounds and fitted by the method of least squares to Bigeleisen's equation  $\ln \alpha = A/T^2 - B/T$ .

## РЕЗЮМЕ

В широком температурном интервале была определена разность давлений пара метиламина, этиламина, пропиламина и их дейтерозамещенных в аминогруппе производных. Используя экспериментальные данные и уравнения реального газа для аминов были вычислены значения коэффициента разделения ( $\alpha$ ) для каждой пары изотопных соединений. Из этих значений  $\alpha$  были получены константы A и B уравнения  $\ln \alpha = A/T^2 - B/T$  методом наименьших квадратов.

## KIVONAT

Meghatároztuk a metilamin, etilamin és propilamin és amino-csoportban deuterizált származékaik közti gőznyomáskülönbséget széles hőmérséklettartományban. A kísérleti adatokból és az aminok viriálegyenleteiből mindegyik izotóp molekulapárra kiszámítottuk a desztillációs dúsítási tényező  $\alpha$  értékeit, amelyeket a legkisebb négyzetek módszerével az  $\ln \alpha = A/T^2 - B/T$  egyenlethez illesztettünk.



## INTRODUCTION

In three previous publications [1,2,3] the results of our investigations of the vapour pressure isotope effects /VPIE/ on water and on successive homologues of the aliphatic alcohol series, chosen as a model of associated liquids, have been reported. The vapour pressure of each alcohol was compared with that of the same compound deuterated at the hydroxyl group.

The investigation of the influence of the molecular structure and C-atom number of the molecule on VPIE have been continued on another group of associating compounds, the aliphatic amines. This paper discusses the experimental results for the primary amines: methyl-, ethyl-, and propylamine. These compounds have an appreciable vapour pressure at room temperature and it is relatively easy to deuterate the amine group to a high D-content.

The absolute vapour pressures of  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{ND}_2$  and  $\text{C}_2\text{H}_5\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{ND}_2$  were determined by Emeleus et al. [4,5] in the temperature range from  $-60^\circ$  to  $-10^\circ\text{C}$ , and from  $-50^\circ$  to  $+10^\circ\text{C}$ , respectively. The vapour pressure difference between  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{ND}_2$  and between  $\text{C}_2\text{H}_5\text{NH}_2$  and  $\text{C}_2\text{H}_5\text{ND}_2$ , respectively, was measured by Wolff and Höpfner [6] in the range from  $-55^\circ$  to  $+20^\circ\text{C}$  with a differential manometric method. Holmberg [7] has determined the VPIE of n-propylamine at the boiling point by Rayleigh distillation. These data cover a relatively narrow temperature range and their temperature dependence are rather inconsistent. To permit the study of the relationship between VPIE and molecular structure it was necessary to determine the VPIE's of methyl- and ethyl-amine over more extended ranges of temperature than those covered by the authors referred to, and the temperature dependence of the VPIE of propylamine was measured, using a differential manometer.

## EXPERIMENTALS

a. Materials: The starting materials were p.a. grade methyl-, ethyl-, and propylamine hydrochlorides. The deuterated amines were prepared by two different methods in order to check the purity of the products.



The first conventional method [4,5,8] was to repeat several times an exchange reaction between the amine hydrochloride species and heavy water, then to liberate the amine with sodium deuterooxide /NaOD/. The amine produced was distilled onto anhydrous CaO and left to stand for several hours.  $\text{NH}_3$  impurity was removed by distillation, and finally the sample was dried with lithium metal.

The second method was isotopic exchange on a gas chromatographic column [9,10,11]. In this procedure the amines obtained from the corresponding amine hydrochloride were deuterated and purified at the same time on a column containing 30 % deuteropolyethyleneglycol. The temperature of the column was different for each different amine and with methyl- and ethylamine a special ampoulebreaking system was employed to feed the column.

The samples with natural isotopic abundance were treated in the same way as the deuterioamines to avoid differences arising from different pre-treatment.

The deuterium content of the labelled amines, analysed by mass spectrometry, was found to be at least 98 atomic percent per amine group.

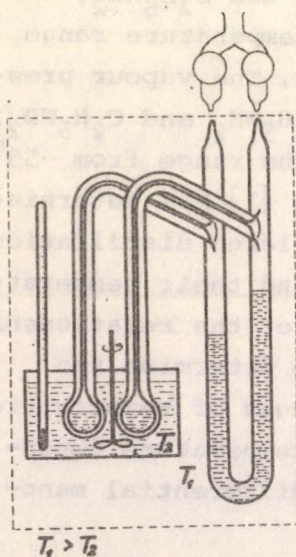


Fig. 1 Apparatus used for the measurement of vapour pressure differences

b. Procedure: The vapour pressure of each deuterated amine was compared with that of the amine of natural isotopic abundance by measuring the difference between the vapour pressures with a mercury differential, which was the full-glass version of an apparatus described elsewhere [2]. Glass balls connected to the manometer by narrow-bore thick-walled glass tubing were used as balance vessels and immersed in a mercury bath to insure that both samples were at the same temperatures /Fig. 1/.

## RESULTS AND DISCUSSION

The vapour pressure differences were measured for  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{ND}_2$  at temperatures from  $-60^\circ$  to  $+30^\circ\text{C}$ , those for  $\text{C}_2\text{H}_5\text{NH}_2$  and  $\text{CH}_2\text{H}_5\text{ND}_2$  between  $-60^\circ$  and  $+90^\circ\text{C}$ , and those for  $n\text{-C}_3\text{H}_7\text{NH}_2$  and  $n\text{-C}_3\text{H}_7\text{ND}_2$  between  $-25^\circ\text{C}$  and  $+65^\circ\text{C}$ .

The experimental data are summarized in Table I, II, and III.

The vapour pressures of the amines with natural isotopic abundance were taken from the manual of Stull [12]. Our experimental points and the curves fitted to them are shown in Fig. 2 along with other data taken from the literature.



Table I.  
Results for  $CH_3NH_2 - CH_3ND_2$

$t$ $^{\circ}C$	$P_H$ mm Hg	$\Delta P$ mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln a$
-60.0	31.2	3.0	10.113	10.088
-55.0	46.0	4.2	9.578	9.546
-50.0	65.0	5.7	9.177	9.136
-45.0	92.0	7.4	8.390	8.251
-40.0	125.0	9.2	7.642	7.585
-35.0	172.0	12.2	7.354	7.276
-30.0	229.0	15.0	6.776	6.695
-25.0	304.0	18.7	6.346	6.251
-20.0	390.0	22.9	6.054	5.945
-15.0	502.0	27.6	5.658	5.535
-10.0	640.0	32.8	5.260	5.123
- 5.0	800.0	38.6	4.947	4.796
0.0	1000.0	45.5	4.661	4.494
+ 5.0	1240.0	52.5	4.326	4.144
10.0	1520.0	59.4	3.990	3.796
15.0	1830.0	67.4	3.750	3.543
20.0	2210.0	76.0	3.499	3.279
25.0	2620.0	84.4	3.276	3.046
30.0	3100.0	93.4	3.063	2.823

Table II.  
Results for  $C_2H_5NH_2 - C_2H_5ND_2$

$t$ $^{\circ}C$	$P_H$ mm Hg	$\Delta P$ mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln a$
-60	8.4	0.75	9.0754	9.0683
-55	12.8	1.05	8.4451	8.4359
-50	18.8	1.40	7.7345	7.7230
-45	27.0	1.90	7.2985	7.2839
-40	39.0	2.60	6.8979	6.8792
-35	54.0	3.30	6.3080	6.2859
-30	74.0	4.30	5.9882	5.9612
-25	100.0	5.40	5.5539	5.5220
-20	130.0	6.50	5.1398	5.1036
-15	172.0	8.10	4.7718	4.7295
-10	225.0	9.50	4.2997	4.2530
- 5	287.0	11.15	4.1221	4.0704
0	360.0	13.70	3.8783	3.8182
+ 5	455.0	16.10	3.6035	3.5368
10	568.0	19.00	3.4021	3.3277
15	700.0	21.80	3.1601	3.0793
20	860.0	24.20	2.8884	2.8034
25	1030.0	25.80	2.5380	2.4521
30	1240.0	28.40	2.3135	2.2237
35	1490.0	31.10	2.1080	2.0147
40	1775.0	33.60	1.9119	1.8162
45	2080.0	36.30	1.7647	1.6662
50	2410.0	38.90	1.6270	1.5266
55	2800.0	40.40	1.4497	1.3505



Table II. (continue)

$t$ $^{\circ}\text{C}$	$P_H$ mm Hg	$\Delta P$ mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
60	3260.0	42.60	1.3116	1.2119
65	3720.0	44.40	1.2029	1.1039
70	4300.0	45.80	1.0744	0.9769
75	4950.0	46.80	0.9457	0.8506
80	5310.0	47.60	0.8961	0.8037
85	6200.0	48.40	0.7870	0.6982
90	7200.0	48.40	0.6778	0.5919

Table III.

Results for  $n\text{-C}_3\text{H}_7\text{NH}_2 - \text{C}_3\text{H}_7\text{ND}_2$

$t$ $^{\circ}\text{C}$	$P_H$ mm Hg	$\Delta P$ mm Hg	$10^2 \ln \frac{P_H}{P_D}$	$10^2 \ln \alpha$
-25.0	23.0	0.90	3.9902	3.9807
-20.0	31.0	1.05	3.4453	3.4348
-15.0	42.5	1.35	3.2279	3.2152
-10.0	56.0	1.60	2.8981	2.8834
- 5.0	74.0	1.85	2.5282	2.5129
0.0	97.0	2.20	2.2938	2.2867
+ 5.0	125.0	2.60	2.0983	2.0794
10.0	158.0	2.90	1.8531	1.8333
15.0	199.0	3.35	1.6959	1.6742
20.0	247.0	3.70	1.5088	1.4864
25.0	302.0	4.15	1.3836	1.3599
30.0	371.0	4.50	1.2206	1.1965
35.0	455.0	4.75	1.0497	1.0256
40.0	550.0	4.90	0.8943	0.8709
45.0	660.0	5.00	0.7602	0.7377
50.0	795.0	4.75	0.5992	0.5796
55.0	940.0	4.35	0.4629	0.4455
60.0	1100.0	3.70	0.3365	0.3223
65.0	1300.0	3.00	0.2308	0.2201

It can be seen that the values obtained by Wolff and Höpfner [6] are for methylamine 6 - 12 % /depending on the temperature/, and for ethylamine 2 - 19 % higher than our values. The results for methyl- and ethylamine obtained by Emeleus et al. [4,5] are strongly scattered and exhibit a rather questionable temperature dependence, while the value for the VPIE of propylamine determined at the boiling point by Holmberg [7] is nearly twice as high as our value.



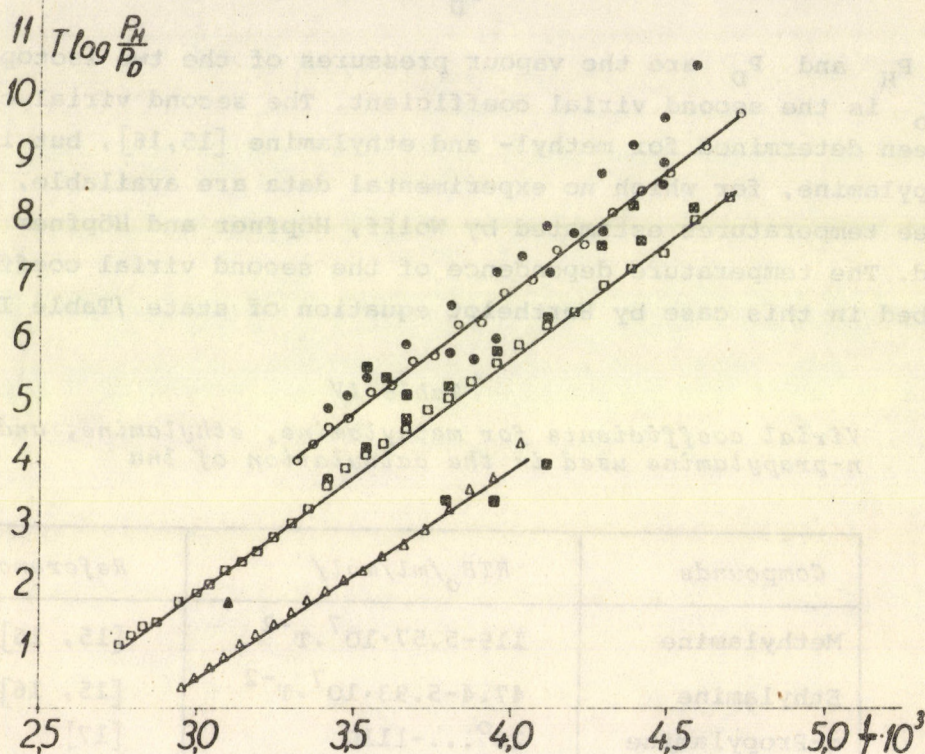


Fig. 2 Effect of deuterium substitution on the vapour pressure of methylamine: ● Emeleus and Briscoe /4/; ○ Wolff and Höpfner /6/; ○ this paper; ethylamine: ■ Roberts, Emeleus and Briscoe /5/, □ Wolff and Höpfner /6/; □ this paper; n-propylamine: ▲ Holmberg /7/, Δ this paper

At moderate temperatures, as shown by Bigeleisen [13,14], the VP/IE can be well approximated by the equation:

$$\ln \alpha = \frac{A}{T^2} - \frac{B}{T} \quad /1/$$

where  $\alpha$  is the separation factor, while A and B are constants which can be calculated from molecular spectroscopic data. It can be seen in Fig. 2 that our experimental data will probably fit Eq./1/ well, so our experimental  $P_H/P_D$  values have been converted into  $\alpha$  values, as described in earlier publications [2,3].

No data are available on the molar volumes of liquid deuteroamines, but since aliphatic amines are very similar to the aliphatic alcohols /in that they also associate by hydrogen bonds/, we expect the molar volume correction terms /in Eq./5/ of [2]/ to be likewise negligible.

For the aliphatic amines the following reduced equation was used:



$$\ln a = \ln \frac{P_H}{P_D} + B_0 (P_H - P_D) \quad /2/$$

where  $P_H$  and  $P_D$  are the vapour pressures of the two isotopic species, and  $B_0$  is the second virial coefficient. The second virial coefficients have been determined for methyl- and ethylamine [15,16], but in the case of propylamine, for which no experimental data are available, the values at three temperatures estimated by Wolff, Höpfner and Höpfner [17] had to be used. The temperature dependence of the second virial coefficient was described in this case by Berthelot equation of state /Table IV/.

Table IV

Virial coefficients for methylamine, ethylamine, and n-propylamine used in the calculation of  $\ln a$

Compounds	$RTB_0$ /ml/mol/	References
Methylamine	$119-5.57 \cdot 10^7 \cdot T^{-2}$	[15, 16]
Ethylamine	$47.4-5.93 \cdot 10^7 \cdot T^{-2}$	[15, 16]
n-Propylamine	$20^\circ \dots -1110$ $0^\circ \dots -1325$ $-20^\circ \dots -1593$	[17]

The values of  $\ln a$  computed with Eq./2/ from the measured vapour pressure differences are presented in Tables I, II, and III and were fitted by least squares method to Eq./1/. The values of the constants A and B are given in Table V.

Table V.

Constants of Equation /1/

Compounds	A	B
Methylamine	9876 $\pm$ 24	24.17 $\pm$ 0.23
Ethylamine	9032 $\pm$ 23	22.87 $\pm$ 0.18
n-Propylamine	8131 $\pm$ 23	23.33 $\pm$ 0.23

The near independence of constant B on the length of the alkyl chain of the amine - as in the case of alcohols of different order - can be understood if one considers that B is connected with shifts in the zero-point energies of the internal vibrations on condensation and is



mainly determined by vibrations of the amine group. The change of constant A reflects the fact that the hindered translation and rotation of the whole molecule depends on the molecular weight and the moment of inertia.

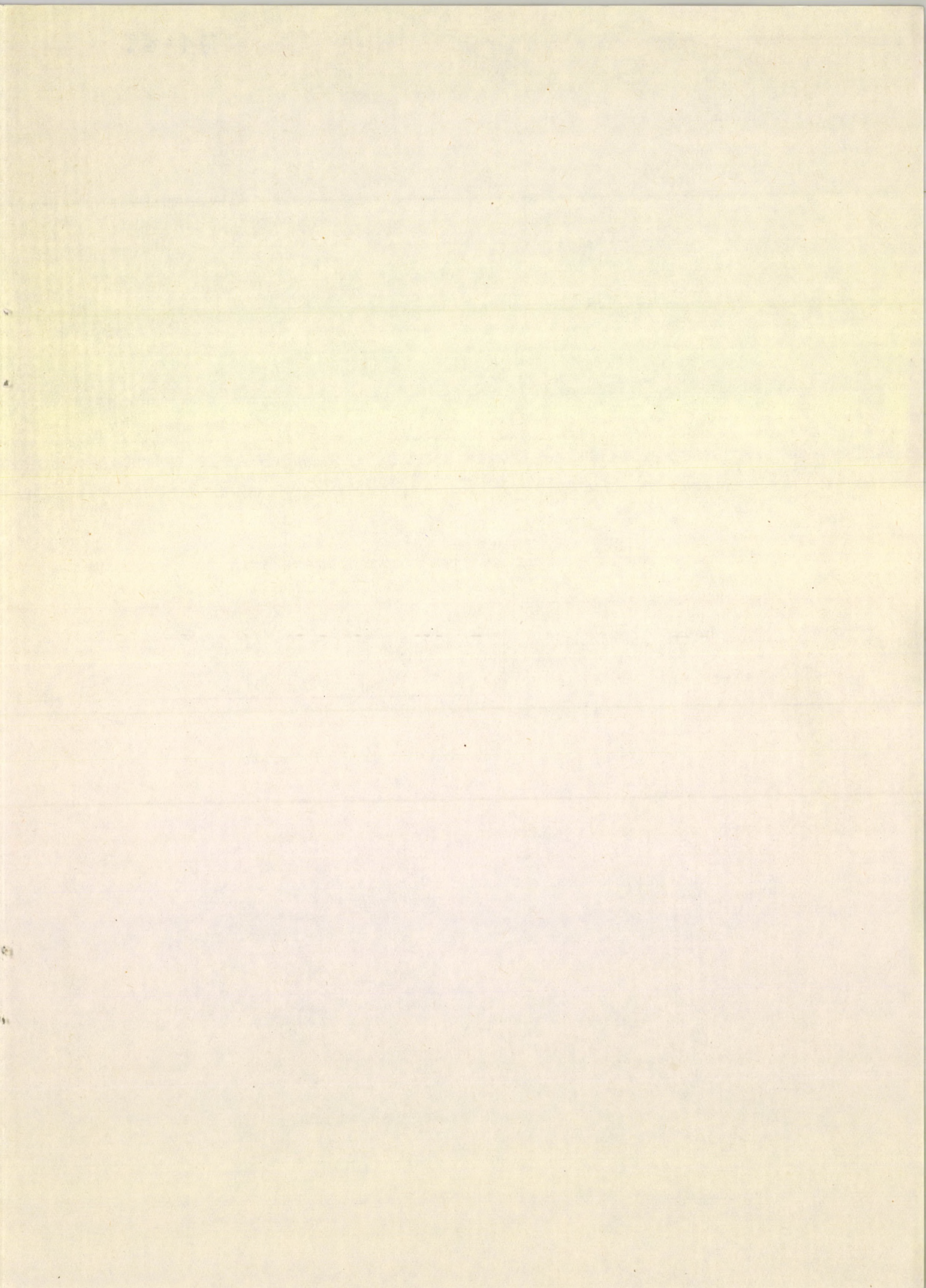
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1971. december hó