tribution in the direction of the correlationfree Holtsmark result.

In judging the magnitude of this effect we want to remember that we have chosen the cut-off at its maximum possible value [15].

Summary

The inclusion of collective long-range effects in the calculation of the electric microfield distribution shifts previous results calculated on the individual variable basis towards the correlationless Holtsmark distribution. For high values of the cut-off parameter and systems close to the critical density the effect may reach 10 per cent. With increasing number of particles in the Debye region the effect disappears. In particular the distribution is little affected in the high field range.

Our findings can therefore not corroborate results which claim decisive effects of the collective phenomena even for high fields and in the far sub-critical region [5].

We are presently studying the analytical interrelations of the procedure and results presented here to similar findings of HOOPER [16] who used an essentially different approach.

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Predictable Low Enrichment of Methane Isotopes by Clusius-Dickel Thermal-Diffusion Columns for Use in Radiocarbon Dating Technique *

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(Z. Naturforsch. **26 a**, 1365—1370 [1971]; received 28 May 1971)

By means of the Clusius-Dickel thermal-diffusion column the range of the radiocarbon dating method may be extended by 20 000 years. It is shown in this work that the total sample amount required is reasonably low, if column dimensions are suitably chosen. The enrichment run time and the length of the thermal-diffusion column will allow sample enrichment in routine operation. Optimal values of column dimensions and operation conditions are calculated.

With an all metal thermal-diffusion column that has been carefully constructed, a high reproducibility is found. The stationary as well as the non-stationary state operation are in agreement with column theory within 1%, concerning the enrichment both of $C^{13}H_4$ and $C^{14}H_4$ in methane. The theory has been evaluated by numerical methods.

1. Introduction

In radiocarbon dating technique the lowest C^{14} activity that can be detected significantly by gas counting methods corresponds to a maximum Libby-age of about 50.000 years B.P. (before present). An outermost limit of about 60.000 years B.P. seems to have been reached by GEYH [1]. In order to extend the radiocarbon dating limit further — especially for establishing a chronology of the interstadials of early WÜRM ice age — we took up anew the problem of enrichment of the C^{14} isotope by known amounts. An enrichment procedure developed earlier in Groningen [2, 3] did not enter routine dating work because the amount of carbon needed and the enrichment time were too high for continuous laboratory work. Therefore we started to develop a more advantageous enrichment plant. In connection with this, the enrichment factors had to be predicted under various conditions of operation.

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* This work is part of a doctoral dissertation at the University of Kiel, 1971.
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[1] M. A. GEYH, Dissertation, Bergakademie Clausthal 1966.

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2. The Enrichment Apparatus

For the enrichment a CLUSIUS-DICKEL thermal-diffusion column [4, 5], working with methane, is used. Methane can reliably be prepared, it has fairly high thermal-diffusion coefficients and very good proportional counter gas qualities. At present, two single columns, each of 2.87 m overall length, are connected in series. We use concentric type columns, which give a greater production rate than hot wire columns at separation factors as needed for our purpose. In order to achieve good reproducibility – a most important feature for analytical application – the columns are built in all metal construction. The diameter of the hot tube is 40 ± 0.05 mm, the width of the separation gap is 6 ± 0.1 mm. Hot and cold tubes are high precision copper tubes (wall thickness 3 mm). In the second column a stainless steel hot tube is used. Coaxiality of hot and cold tube is warranted by radial spacing cylinders (2 mm diameter, steel), three at every 50 cm column length. The cylinders are fixed in the cold tube wall. The cold tube is supported by the outer cooling water jacket (steel, 84×4 mm) and is kept under tension of about 900 kp. The linearity of the cold tube wall is controlled by three adjusting screws at mid height. They are set by help of an optical method to within ± 0.07 mm. The total deviation from a perfect linear tube is estimated to be less than 0.2 mm. Each column is heated by eight heating rods ($7^{\Phi} \times 2450$ mm, power consumption max. 200 Watt each). They are arranged coaxially to the hot tube by ceramic multiple hole tubes which are fitted to the inner hot tube diameter. In this way a highly homogeneous temperature distribution on the hot wall is aspired. The columns are supported by cardan joints and the vertical adjustment is better than 1 : 2500. The column bearing shelf is cushionned twice by rubber bumpers.

The gas flow system consists of the two columns connected in series, and a storage vessel, for the present of 85 l content, that is connected to the negative column end by means of a thermal convection loop. For inter column gas exchange a gas swing volume [6] is used.

Up to now the working gas is tank methane that is purified over liquid nitrogen cooled active charcoal. The remaining nitrogen concentration is less than 50 ppm. The column performance is investigated on the $C^{13}H_4$ isotope that is analysed bv a CH4-ATLAS mass spectrometer with single collector technique. Later on enrichment of artificial $C^{14}H_4$ has been studied, too, by proportional counting.

3. Experimental Results * – The Stationary Case

The separation tubes are investigated first in stationary state operation. With both ends closed equilibrium is reached within 6 to 8 hours and the isotope is then distributed along the separation tube according to

$$c/(1-c) = S\, e^{2A \cdot z}$$

(c = molar fraction, z = longitudinal coordinate). The constant of integration, S, is determined by conservation of the total amount of the isotope under consideration. The factor $2A$ (we use the notation of FURRY, JONES, and ONSAGER [7]) – the reciprocal of the characteristic separation length Λ – was determined from the initial molar fraction and the stationary state molar fraction at the positive column end ($z = L$, L = column length). $2A$ is dependent on gas pressure according to

$$2A = \frac{\beta\, p^2}{1 + (\gamma_{\text{th}} + \gamma_{\text{P}})\, p^4}\,.$$

γ_{th} is the theoretical value, γ_{P} takes account of some remixing effects due to parasitic convection caused by constructional inadequacies. The $2A$-p-dependence has been verified in the pressure range from 0.3 to 1.5 atm. The pressure at $A_{\max}$ is about 0.8 atm at 300 °C hot wall temperature. The root mean square deviation of the experimental points from a least square fit is 0.5 to 0.8% (Fig. 1). These values demonstrate the reproducibility of column operation, too. The coefficients β and $\gamma = (\gamma_{\text{th}} + \gamma_{\text{P}})$ are obtained by an iterative least square fit. γ is given in Table 1, column 4, denoted as $\hat{\gamma}$.

In Table 1, column 5, γ_{th} is computed from the theory of thermal-diffusion columns as given by FURRY and JONES [8]. Comparing the experimental and theoretical values, separation tube S I is a fairly good approximation to the perfect separation column, whereas in tube S II some remixing effects take place. These may be caused by an azimutal inhomogenity of the stainless-steel hot wall temperature distribution caused by insufficient fitting of the heating system ceramic tubes to the hot tube wall, that could not be avoided for technical reasons.

From experimental β values the thermal-diffusion factor α of the system $C^{13}H_4 - C^{12}H_4$ can be derived. This quantity is predicted by gas theory with poor accuracy only. Weighing the significance of α-values

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* The *enrichment factor* of a gas quantity is the ratio of the actual molar fraction to the initial one. The *separation factor q* is defined by $q = c_+\,(1-c_-)/(c_-\,(1-c_+))$, where c_+, c_- are the molar fractions at the positive resp. negative end of the separation column.

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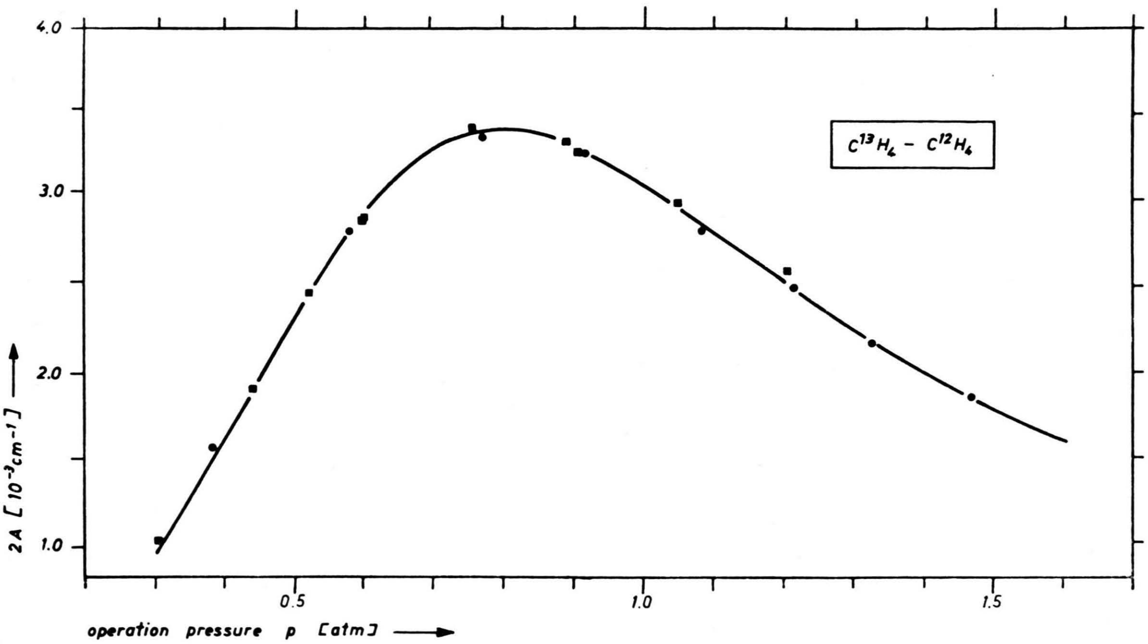

Fig. 1. Experimental values of $2A$ varying with operation pressure. $2A$ is related to the equilibrium separation factor q according to $\ln q = 2A \cdot L$ (L=column length) (column SI, temperatures: 12 °C/295 °C).

derived from column experiments one must realize that parasitic remixing disturbances affect β far less than γ [9, 10]. Moreover their influence may be estimated from γ_P. Since the temperature difference ΔT responsible for thermal diffusion cannot be considered small ($\Delta T/T \approx 1$) a suitable temperature dependence for $\alpha = \alpha(T)$ must be chosen [11], the coefficients of which are obtained by a fitting procedure from the experiments. With

$$\alpha = A + B\ln(T^*), \quad \text{where} \quad T^* = T/152.8,$$

T^* = reduced temperature, T = abs. temperature, we got – using the Furry-Jones theory for computing $\beta_{\text{th}} = \beta_{\text{th}}(A,B)$ –

$$A = (-1.59 \pm 0.04) \cdot 10^{-3},$$
$$B = (+8.87 \pm 0.65) \cdot 10^{-3}.$$

(For the temperature range see Table 1.) Especially we found

$$\alpha(C^{13}H_4 - C^{12}H_4) = (7.27 \pm 0.05) \cdot 10^{-3} \quad \text{at } T = 414\ {}^\circ\text{K}.$$

The absolute error is that of the quantity $\varrho/(\eta \cdot D_{12})$ (ϱ = density, η = viscosity, D_{12} = ordinary binary diffusion coefficient) and is estimated to about 3 to 5%. This is essentially the error, which D_{12} might have. It gives the main portion to the overall error of α. – The approximation for $\alpha = \alpha(T)$ may be refined, if more measurements become available.

Table 1. Convective remixing coefficient γ. Comparison of experiment ($\hat{\gamma}$) and theory (γ_{th}).

1	2	3	4	5	6
column	T_{cold} °C	T_{hot} °C	$\hat{\gamma} \pm \sigma_{\hat{\gamma}}$ atm^{-4}	γ_{th} atm^{-4}	$\frac{\hat{\gamma} - \gamma_{\text{th}}}{\gamma_{\text{th}}}$ %
S I	12	295	2.459 ± 0.029	2.366	3.9 ± 1.2
S II	12	275	3.475 ± 0.048	2.808	23.8 ± 1.7
S II	12	358	2.384 ± 0.030	1.877	27.0 ± 1.6
S II	13	417	1.703 ± 0.031	1.362	25.0 ± 2.3

4. Experimental Results – Non-Stationary Case

The development of the concentration distribution of a multi-isotope mixture in a thermal diffusion

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column[12, 13] is described by a system of quasilinear partial differential equations of parabolic type, that reduces for a binary mixture to essentially one equation[14], that we call the *column equation:*

$$-\mu c_t = H c_z (1-2c) - (K_c + K_P + K_d)\, c_{zz},$$

μ = mass per column unit length, H, K_c, K_d, K_P = transport coefficients, c = molar fraction of the isotope under consideration, t = time, z = longitudinal parameter, c_t, c_z, c_{zz} = partial derivatives.

To compare theory and experiments in the non-stationary state we evaluated this equation by means of an implicite finite-difference scheme. Reservoirs, even the small constructional volumes at both column ends, have been taken into account within the boundary conditions. The coefficients H, K_c and K_d were computed from theory using the $\alpha(T)$-dependence derived from stationary state measurements. K_P is related to γ_P by $K_P = \gamma_P \cdot K_d$, γ_P taken from equilibrium measurements, too. Without fitting parameters further, the time dependence of $C^{13}H_4$ enrichment factor observed at the positive column end agrees with the calculated one within 0.3% (root mean square difference), for column with both ends closed off as well as for operation with the 85 l reservoir at the negative end (Fig. 2). Herewith the theoretical value of K_d that cannot be derived from equilibrium state, is confirmed.

Operating the columns connected in series the gas exchange between the columns is controlled by the operation conditions of the gas swing volume. This may be described by a gas exchange resistance the proper value of which is taken from experiment. In a long time run lasting 350 h the positive end enrichment factor has been pursued, withdrawing one or two samples per day. The rms deviation of experimental points from the calculated curve is 0.8%.

C^{14} enrichment has been investigated with the two-stage column arrangement with negative end reservoir. To do so, the content of both columns was mixed when the run was terminated and the mean or integral C^{14}-concentration was determined in a 3 *l* proportional counter as used for C^{14}-age-determinations. Beside this the depletion of the negative end

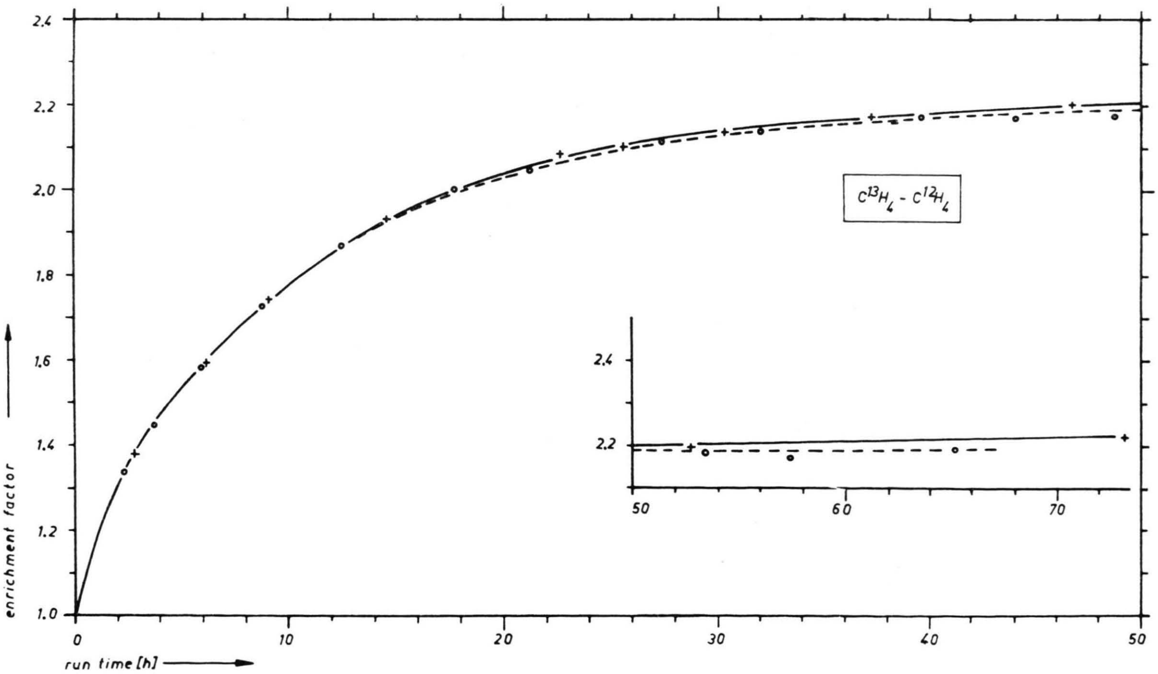

Fig. 2. Approach to equilibrium of $C^{13}H_4$ enrichment at the positive column end. The curves are calculated from theory (column SI with negative end reservoir, temperatures: 12 °C/292 °C. + series SI/23 at 0.770 atm, ○ series SI/24 at 0.759 atm operation pressure).

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reservoir was measured. Simultaneously all measurements were done for the $C^{13}H_4$ species, too. In three separate runs the most extreme differences between experimental and calculated values were $+0.32\%$, -0.48%, and $+1.55\%$ in $C^{13}H_4$ enrichment factor and -0.88%, $+0.01\%$, and $+0.32\%$ in C^{14} enrichment. — Maximum C^{14} enrichment factor obtained was 3.4 after 4.8 d run time.

In calculating C^{14} enrichment a ternary isotope mixture is considered. The thermal-diffusion factors of the binary sub-systems $C^{14}H_4-C^{12}H_4$ and $C^{14}H_4-C^{13}H_4$ are derived from the thermal-diffusion factor of the system $C^{13}H_4-C^{12}H_4$ taking into account the modified relative mass differences.

5. Calculating the Transport Coefficients of the Column Equation

For calculating the transport coefficients H, K_c and K_d from thermal-diffusion column theory, essential use is made of the temperature dependences of α (thermal-diffusion factor), D_{12} (coefficient of binary concentration-diffusion), η (viscosity) and λ (heat conductivity). Reliable data especially at higher temperatures are not known, therefore we calculated the gas quantities from theory, for a temperature range from 0 °C to 450 °C. Viscosity and ordinary diffusion are known to be given by the Chapman-Enskog rigorous gas theory of monoatomic molecules with fairly good accuracy [15–17]. The deviations of theory from literature data are 0.5% for η and about some percent in case of D_{12}, the temperature range being 0 °C to 100 °C. We used a modified Buckingham-(Exp-6)-model with parameters [18, 19]

$$s=14, \quad \varepsilon/k=152.8\ {}^\circ\mathrm{K}, \quad r_m=4.206\ \text{Å}$$

and calculated η and D_{12} in the second approximation according to CHAPMAN [20]. In calculating λ rotational energy states must be considered. We use a modified Eucken formula and take into account energy exchange between translational and rotational states following a suggestion of MASON [21]. The temperature function of the specific heat is derived by interpolation of experimental data [22]. The λ values obtained lie in the upper range of literature data, the spread of which is some % at least.

Once the temperature functions of the gas quantities are known the H, K_c, and K_d coefficients are easily calculated from theory [23] by multiple integration over the temperature distribution in the separation gap. Up to temperatures as used here the temperature distribution is determined by heat conduction alone. Power consumption is in good agreement with calculations from thermal conductivity.

6. The Optimation of the Enrichment Plant

The enrichment plant is to produce an enriched quantity sufficient for filling the proportional counter of the dating equipment. By optimation the product costs are to be kept low. We will only consider costs necessary for physical reasons, i. e. costs of heating power and cooling water. Costs for providing natural C^{14} samples and for chemical pretreatment are taken into account by driving the enrichment plant up to high isotope yield — typically we demand a yield of 80% — so that the sample size to deal with will be as low as possible right from the beginning.

Optimation now means to find those dimensions and operation conditions that make the quantity $l\,t\,q$ ($l=$ column length, $t=$ run time, $q=$ heating power consumption per column unit length) minimal. With finit total sample size the operation conditions and column cross section parameters (pressure and temperature, separation gap width and hot tube radius) cannot be optimized independently from the column length and from the size of the end reservoirs, as would be possible with the negative end open [24].

For optimation at first the optimal column length and the optimal run time are determined with operation conditions, isotope yield, and column cross dimensions fixed, to give the lowest $l\,t\,q$-value. By further varying operation conditions and column dimensions the variation of the $l\,t\,q$-product is studied. For these calculations a sample size of 1.8 g CH_4 is assumed, 12-fold enriched in C^{14}. Without enrich-

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ment this sample size allows to date back to 50.000 years B.P.

The computations show the costs to be lower if – at high isotope yield – no additional positive end reservoir is used but the sample is withdrawn by separating a proper length of the column and mixing the gas in it.

The hot tube temperature should be as high as thermal stability of the methane molecule will allow (i. e. 400 °C to 450 °C). – The *l t q*-value becomes lower with smaller hot tube radii (at least in the range from 15 to 30 mm), however, the run time increases thus reducing sample flow in routine work. Furthermore the costs decrease with decreasing separation gap widths (4 to 8 mm investigated) – and correspondingly higher operation pressures. However the gap width is determined by technical rather than economical arguments. At small gap width the influence of low adjustment accuracy will strongly increase parasitic remixing effects and diminish reproducibility. Furthermore operating pressures become too high for laboratory handling.

With a separation gap width of 6 mm and a hot tube radius of 20 mm the operation pressure amounts to 1.25 atm, at 400 °C hot tube temperature and isotope yield of 80%. The sample, 1.8 g CH_4, enriched in C^{14} by a factor of 12, is obtained in 8.5 d. The column length is 9.24 m, taking 4.00 m for gas withdrawal. The total gas amount is 27 g. By lower isotope yield predominantly the run time is shortened. With 60% yield the operation pressure is 1.34 atm, the run time 5.0 d, the column length 8.10 m and the withdrawal length is 3.73 m.

7. Extending the Range of the Radiocarbon Dating Method

Statistics of radiocarbon dating show that maximum age, which is determined by the lowest sample activity significantly separable from background, will be increased by C^{14} enrichment by

$$\Delta T = \tau \cdot \ln(m),$$

($\tau = C^{14}$ life-time $= 5730 \pm 40$ a, $m =$ enrichment factor), e. g. by about 20.000 years by 12-fold enrichment.

To extent the radiocarbon dating limit further the problem is not to achieve a greater C^{14} enrichment – once the greater technical effort is accepted – but to be sure to have samples quite free from any contamination of younger C^{14}. This might limit the application of the enrichment procedure in practice. An ultimate limit will be given by post-mortem C^{14} production from N^{14} of the sample itself by cosmic ray neutrons and other natural neutron sources.

For younger samples enrichment improves the accuracy of age determination. This improvement decreases with lower sample age. Because of the high activity of young samples – even without enrichment – the sample net counting rate does not contribute considerably to the age error, which predominantly is determined by the errors of the reference quantities, i. e. background and modern natural radiocarbon standard. A guide-line for the lowest age T_m, for which enrichment is still efficient, is

$$T_m = \tau \cdot \ln(m \cdot r/n)$$

$r =$ modern natural radiocarbon standard, not enriched, $n =$ background, $m =$ enrichment factor.

Typically, T_m is of the order of 10.000 to 30.000 years ($m = 12$).

Acknowledgements

I thank Prof. Dr. E. Bagge and Dr. H. Willkomm heartily for their stimulating interest on this work. Financial support given by the Bundesministerium für Bildung und Wissenschaft is gratefully acknowledged. – The computer calculations have been performed at the Rechenzentrum der Universität Kiel.