

NIZHNY NOVGOROD STATE TECHNICAL UNIVERSITY N.A. R.E. ALEKSEEV

Химики без _{смср}границ

Prof. Ilya V. Vorotyntsev

Nanotechnology and Biotechnology Department



Laboratory of Membrane and Catalytic Processes



Окружающий Мир это дружественная или враждебная среда?

Почему мы боимся химии?



Почему мы боимся химии?



Нильс БОР



На свете есть
 столь серьезные
 вещи, что
 говорить о них
 можно только
 шутя...

Химия вокруг нас...



















Всё, что нас окружает – это химия!







ФАНТАСТИКИ Ф АРТУР КЛАРК

Артур Клари Конец-дет гва

> Any sufficiently advanced techn ology is indistinguishabl e from magic*

3BE3IN

ронтаны рая

Артур Кларк КОСМИЧЕСКАЯ ОДИССЕЯ 200<u>1 го</u>да

Сэр Артур Чарльз КЛАРК

* «Любая достаточно развитая технология неотличима от волшебства»

Электроника – неотъемлемая часть нашей жизни!

Электроника – «мозг и нервная система» высокотехнологичных изделий всех отраслей мировой индустрии!



























Наномашина на золотой поверхности. Изображение

D IL

E

31

T

5

Nobel Prize 2016



Лауреаты Нобелевской премии по химии 2016 года: <u>Жан-Пьер Соваж</u> (Jean-Pierre Sauvage), <u>Фрейзер Стоддарт</u> (J. Fraser Stoddart), и Бернард Феринга (Bernard L. Feringa). Изображение с сайта cen.acs.org



Illustration: @Martin Högbom/The Royal Swedish Academy of Sciences

Nobel Prize 2017



Рис. 1. Лауреаты Нобелевской премии по химии 2017 года. *Слева* направо: Жак Дюбоше, Йоахим Франк и Ричард Хендерсон. Фото с сайта <u>sciencenews.org</u>

НЕ НОБЕЛЕВСКИЙ ЛАУРЕАТ







АЛЕКСАНДР НЕВСКИЙ



Общий рейтинг

		всего голосов	место
	Александр Невский	524 575	1
	П.А. Столыпин	523 766	2
	И.В. Сталин	519 071	3
	А.С. Пушкин	516 608	4
	Петр I	448 857	5
	В.И. Ленин	424 283	6
	Ф.М. Достоевский	348 634	7
	А.В. Суворов	329.028	8
	Д.И. Менделеев	306 520	9
	Иван 1V грозный	270 570	10
	Екатерина II	152 306	11
	Александр II	134 622	12

Ontons Quetante ancours malige, ac ... & anage way & warmane flit a signa - for D. Manden A. Le. 1:-12 Ke= 90 ?= 100 N6=94 Ja-189 1=51 GESE 11.16 10 - 16 lass' 14-1194 Ht-1924 K= 50 Qu= 144 2-191. Kalinsy. H=1.86 (3499. H=1. ?= 8 1= 12 Garbay . 10=101 Kon IN. light dente headigt Biall. 20 winof D Q= 2,4 .1=68 11=116 . ta= 19%. 1:=11 Care Jin 18 1 = 10 In -118. 1=31 .41= A No 14 8= 188 A: \$10 ! 1= 12 10 - Fur a= 455 A1 = 80 C=16 Jea 189 Je= 128! F=1 d= 455 h= 10 2-147. N=23 K=39 R1-154 G=13 H-201. Niep listo desigt hant Phat 21%. ?= 45. Galt : ciast! the 14 th 60 \$ 195 Maljo ai C Essai Vune fistine Amo to Robie des dements Vapris leves poils chamiques at the minutes in the sections of iniques from D' a line the section of the sectio NT incomo. J8 # 6.9. Inance and more - ----Korne ioi way - . 4 Ancesis, no esterno, Iner delike ut ine. ander he wery, & Tomor hand had sopring of -

Первый набросок Таблицы…



& Merdand

H AND AND				
Md ¹⁰¹ 2019				
M.O.				
2 have 37 and and				10
Sannage and a manual and the san gove				10
Tines Health 2 - 14 V= 51 - Marte Tarlan			the second	
Gase days W. M.			IIIA IVA V	VIA VIIA
Kallard Ralling Bally		B		TO SEE TO NO.
Analy dente service Branche to	7 4 4 40	11 12 A	13 51 14 P	15 000 16 000 17 000 18 S 11 Cl 11 Ar 18
North Sinds 25 W. Sandth.		18 118 ****	· 11 James 32 House	10 10 10 10 10 10 10 10 10 10 10 10 10 1
Frit de la Martin Call	Mo Fe Co INI		Ge As	Se THE Br THE Kr THE
Parto dange and a	TE Ry TRA	Ag Cd III	49 Sn Sb	Te State State State
1 the 60 th all the for	the Do Str "ZPL		Pb BI	
tillene d' and an a	and the second second	10 mar 112	and the second second	Tentor Tento Litto
and a start of a start of the start of the	In M. M. Or	En Cn	Uut Fill Uu untram Panonjur anuma	p LY Uus Uuo
	A State of the second	The second	EF STA	
		and the second	10 II II	
		Er Im salto	Lu - E	



The first congress of Russian naturalists

ПЕРВЫЙ МЕНДЕЛЪЕВСКІЙ СЪЪЗДЪ по общей и прикладной химіи въ с.-петербургъ. 1907.

Билеть глена Съпьзда

Димопроизводитель Распорядительного Комитета Съизда



Этоть биреть служить удостовбреніемъ для входа на всё засбданія Събада.

RUSSIAN CHEMICAL SOCIETY n.a. D.I. Mendeleev

. hyping ou he Decapacions for the Colling that and the to an and marked proceed and the colling that the state . Aligned marked as any more than any marker . Marked marked Chagants

C. Sundandering Bogarden Bogarden Bogarden Bogarden Bogarden A. Maawale Bogarden B. Sundan B. Su

A. Uly war

Junch Gutan Sumantan Usycenta

February 1868 - sketch of the main provisions of the Charter

1907 - the first Mendeleev Congress on General and Applied Chemistry

NUMBER OF MEMBERS OF THE RUSSIAN CHEMICAL SOCIETY





YOUTH COMUNITY A NEW STAGE OF CHEMICAL SOCIETY n.a. D.I. Mendeleev

Together with the whole planet!





40000 PARTICIPANTS FROM 188 COUNTRIES



IYCN











WELCOME

Laboratory of membrane and catalytic processes



www.lmcp.today

604050, Nizhny Novgorod, Minina Street, 24





Prof. Ilya V. Vorotyntsev



Professional. International. Innovative







MATERIAL SCIENCE

CHEMICAL ENGINEERING

NEW MEMBRANE
 MATERIALS
 (Polymeric and ceramic)



INTENSIFICATION OF MEMBRANE PROCESSES (Cascades, new module)



HYBRID PROCESSES (Membrane contactors,

Membrane Absortion)



APPLICATIONS OF MEMBRANE GAS SEPARATION





fraction

OUR SEPARATION AND PURIFICATION TECHNOLOGIES





SCHEME OF MEMBRANE GAS SEPARATION MODULE AND RECTIFICATION COLUMN





THE RADIAL COUNTERCURRENT MEMBRANE MODULE:



CHARACTERISTICS OF THE MEMBRANE MODULE

THE DEPENDENCE OF THE SEPARATION FACTOR FOF THE DEGREE OF SEPARATION MONOGERMANE (GeH₄) FROM WATER (H₂O)



1 – calculation according to the model of ideal displacement;
2 – calculation according to the model of complete mixing;
3 – experimental data

// Desalination. 2006. 200 (1-3) 232-233. DOI: 10.1016/j.desal.2006.03.307 // Desalination. 2002. 146 (1-3) 249-254. DOI: 10.1016/S0011-9164(02)00482-4



CASCADE OF MEMBRANE MODULE WITH FEEDING RESERVOIR (FD)



1 – feeding reservoir (FD); 2 – pressure reducer; 3 – membrane module; 4 – vacuum-compressor

$$\mathbf{f} = \frac{C_0}{C} = \left(\frac{N_0}{N}\right)^{F^{-1}}$$

 N_0 – quantity mole of the mixture in a FD at initial time, N - quantity mole of the mixture in a FD after purification

Vorotyntsev V.M. et al . Petroleum Chemistry 2011 51 (8) 595-600. Vorotyntsev V.M. et al . Inorg. Mat. 2009 45 (11) 1263–1266. THE DEPENDENCE OF PURIFICATION RATIO FROM QUANTITY OF SAMPLED SUBSTANCES MIXTURE: R-12 (CF_2CL_2) – IMPURITY OF R-218 (C_3F_8)= 2.94



Quantity of picked gas, %

1 – membrane module with a feeding reservoir;

2 – single membrane module



PRACTICAL APPLICATION FOR ISOTOPE SILANE PURIFICATION

FAST-PERMEANT IMPURITY DEPLETION LOOP



The silane product is concentrated in the feed tank via recirculation of the retentate, and the impurity is concentrated on the smaller loop which discharges to the impurity storage. The imply can be recycled as feed (dashed – dotted line).

Valmor F. de Almeida, Kevin J. Hart, Journal of Membrane Science, V. 527, 2017, P. 164-179



EXPERIMENTAL SLOW-PERMEANT IMPURITY DEPLETION LOOP CURRENTLY IN TESTING

doi.org/10.1016/j.memsci.2016.12.049

MEMBRANE CASCADE TYPE OF «CONTINUOUS MEMBRANE COLUMN»



ONE-COMPRESSOR ONE-/TWO- STAGE MEMBRANE APPARATUS FOR AMMONIA-BASED MIXTURES SEPARATION



SEPARATION FACTOR:

$$F^{-1} = \frac{C_{1.1}}{C_{1.0}} = \left(\frac{L_{1.0}}{L_{1.1}}\right)^{(\alpha^* - 1)/\alpha^*}$$

ideal mixing regime

PURIFICATION DEGREE:



ONE-COMPRESSOR MULTISTAGE MEMBRANE APPARATUS

PURIFICATION DEGREE



I.V. Vorotyntsev et al. Petroleum Chemistry (2017) 57 (2) 172-181



MEMBRANE SEPARATION + DISTILLATION UNDER ELEVATED PRESSURE

8÷12 atm 18÷25°C Reflux condencer Cut-off fraction Optional radial membrane module Retentate flow Permeate flow Compressor NH, NH₃ feeding reservoir TOTA Film evaporator 0 **Bottoms** fraction





Retention Time (min)

MEMBRANE SEPARATION + DISTILLATION UNDER ELEVATED PRESSURE

Two-dimentional GC-PDHID|TCD analytical system for [sub-ppm \div 100%] determination of H₂, O₂, N₂, CH₄, CO, CO₂



M.M. Trubyanov et al. Journal of chromatography A (2016) 1447 129-134



Concentration, ppm

Intensity, T %

ANALYTICAL CONTROL OF THE PURIFICATION PROCESS. GAS CHROMATOGRAPHY



 $NH_3 + H_2O$



EXAMPLES OF UNSTEADY-STATE PERIODICAL SEPARATION TECHNIQUES



PRESSURE SWING ABSORPTION

MEMBRANE SEPARATION







time duration



BATCH DISTILLATION WITH PERIODICAL WITHDRAWALS

Kinetics of concentrating and ultrapurifying dichlorosilane by batch distillation with periodical withdrawals



V.M. Vorotyntsev et al., Theoretical Foundations of Chemical Engineering, 2007



UNSTEADY-STATE MEMBRANE GAS SEPARATION BY CONCENTRATION PULSE

PULSED INPUT OF THE FEED MIXTURE



- Separation on nonselective membrane
- Increase in selectivity for **diffusioncontrolled** separation
- Decrease in productivity



UNSTEADY-STATE MEMBRANE GAS PURIFICATION BY PERIODICAL WITHDRAWALS

Working principle of Pulsed retentate operation



Removal of highly penetrating impurity



Theoretical modeling



Separation factor (pulsed mode)

$$F' = \frac{C_{in}}{C'_{out}} = \left(\frac{L_{in}}{L'_{out}}\right)^{\alpha^* - 1}$$

$$\alpha^* = \alpha / 1 + (\alpha - 1) \frac{P_2}{P_1}$$

 C_{in}/C_{out} - inlet and outlet concentrations ratio; L_{in} , L_{out} , L_{perm} - inlet, outlet, permeate fluxes; α - ideal selectivity; α^* - effective selectivity; P_2 and P_1 - permeate and feed pressure



Efficiency vs productivity compared to steady-state



EXPERIMENTAL SETUP FOR UNSTEADY-STATE MEMBRANE GAS SEPARATION





Nitrogen-based model mixtures and GC conditions

A N

Gas Q (Barer)		α _{id}	α _{ef}	
N ₂ 200±5		-	-	
CH ₄ 550±15		2.75±0.15	2.7±0.5	
CO2	1800±50	9.0±0.5	7.5±1.5	
N ₂ O	2400±70	12.0±0.7	10±2	
Component of the GC		Characteristics		
Detector		TCD, 100mA, 100°C		
Chromatographic	column	Porapak Q, 60/80 mesh, 80°C		
		2 m × 3 mm i.d. stainless steel tube		
Sample loop		3 ml, 80°C		
Carrier gas		He 99.9999%, 30 ml/min		

High-efficient radial membrane module in countercurrent mode:



low variation of the gas linear velocity helps to provide the laminar gas flow eliminates any trapped gas or dead zones

SYSTEM DESCRIPTION

Membrane

Poly(arylate-siloxane) Silar®

Gas mixture

 N_2 : $N_2O = 1$: 0.01 $\alpha_{ideal}(N_2O / N_2) = 12.0 \pm 0.7$

Operational parameters

- Stage cut
- Pressure ratio
- $\Delta \tau_{\rm open}$ duration of withdrawal
- $\Delta \tau_{close}$ duration of stripping $\Delta \tau_{total}$ total cycle duration
- Sample amount ratio





PRELIMINARY EXPERIMENTAL RESULTS

COMPARISON OF A PULSED MODE AND A STEADY-STATE MODE



DETAILED EXPERIMENTAL VERIFICATION

SEPARATION OF BINARY MIXTURES IN RADIAL COUNTERCURRENT MEMBRANE MODULE IN TWO REGIMES



APPROACHING CLOSED MODE OPERATION



Remarks

- Separation efficiency increases with the increase of stripping time
- With the increase of stripping time the system approaches closed mode operation
- Smallest retentate sample volume provides the highest separation efficiency

OPTIMIZATION PERSPECTIVES



Separation performance of a pulsed retentate operation for different cycle times at constant productivity (opening to closing time ratio is 1/3).

- SAME productivity $\Delta \tau_{open} / \Delta \tau_{total} = 1 / 3$
- increasing amounts of withdrawn samples

NON-MONOTONIC DEPENDENCE

mutual influence of the amount of withdrawn sample and the stripping time



UNSTEADY-STATE MEMBRANE GAS SEPARATION WITH PERMEATE RECYCLE FOR LOW PERMEABLE COMPONENT CONCENTRATION SETUP





Principal scheme of unsteady-state membrane gas separation with permeate recycle for Low permeable component concentration setup

V.V





Separation efficiency is higher for whole range of withdrawal rate Significant increase in separation efficiency at decreasing productivity

p=L_{out}/L_{in}

1 Minimum productivity

Maximum productivity



PRELIMINARY EXPERIMENTAL RESULTS



g.



A hybrid hydrate-membrane process for CO_2 recovery from flue gas in the presence of THF as additive. Hydrate formation is carried out at 273.75 K and 2.5 MPa in the three stages.



CASCADE OF MEMBRANE MODULE + GAS HYDRATE CRYSTALLIZATION

SCHEME OF THE HYBRID GAS HYDRATE-MEMBRANE SEPARATION METHOD



P. Linga, A. Adeyemo, and P. Englezos // Environ. Sci. Technol., 42(2008), 315–320



CATALYST PREPARATION PROCEDURE

NiCl₂ · 6H₂O → NiCl₂ + 6H₂O[↑] (T = 873 K, fast heating, 10 min) NiCl₂ · 2H₂O → NiCl₂ + 6H₂O[↑] (T = 473 K, p = 5 · 10⁻³ bar, 4 h) NiCl₂ + H₂ Ni + 2HCl[↑] (T = 473 K, HCl/H₂ = 1.5, 3 h)

Compound	Flammability	Explosive	Toxicity	
SiCl ₄	1	2	4	
GeCl_4	1	2	4	
SiHCl ₃	4	2	4	
SiH ₄	4	3	2	
GeH ₄	4	3	4	

ENERGY SAVING CATALYTIC PROCESSES

REACTION MECHANISM



CHARACTERISTICS OF THE SYNTHESIZED CATALYST

Symbol	Diluents / (%v/v, Tol/Hep)	Specific area / m²·g ⁻¹	Average pore diameter / nm	Particle average diameter / µm	Exchange capacity / (meq/ml)
2M5VP-t	100/0	8.012	31.862	302	4.5
2M5VP-t/h	90/10	9.043	32.024	338	4.8
2M5VP-h/t	50/50	28.15	80.418	362	5.3

2M5VP-h/t

2M5VP-t



2M5VP-t/h

SEM micrographs of the 2M5VP resins with the different porogen



Будучи химиком, Герман Фогель знал, как сделать бомбу! На самом деле большая часть его курса обучения была посвящена тому, как не сделать ее по ошибке...

«Химия занимается веществами, а не телами» **Д.И. Менделеев**





НИЖЕГОРОДСКИЙ ГОСУДАРСТВЕННЫЙ ТЕХНИЧЕСКИЙ УНИВЕРСИТЕТ им. Р.Е. Алексеева ФЕДЕРАЛЬНЫЙ ОПОРНЫЙ УНИВЕРСИТЕТ

НГТУ в социальных сетях



FACEBOOK.COM/NNSTU/



VK.COM/NNTUALEKSEEVA









INSTAGRAM.COM/NNTU.ALEKSEEVA

