NUMMER 1793 5 FEBRUARI 1938 35e Jaargang, No. 6

CHEMISCH WEEKBLAD

ORGAAN VAN DE NEDERLANDSCHE CHEMISCHE VEREENIGING EN VAN
DE VEREENIGING VAN DE NEDERLANDSCHE CHEMISCHE INDUSTRIE

Hoofdredacteur: Dr. W. P. JORISSEN, Leiden, Zoeterwoudsche Singel 18
(part. adres: Hooge Rijndijk 15, telefoon 1449, postrekening 3569).

Redactie-Commissie: Dr. A. Bloemen (secretaris), Dr. C. A. Lobry de Bruyn, Dr. G. C. A. van Dorp
Dr. C. Groeneveld en Dr. Ir. J. A. M. van Liempt.

N.V. D. B. CENTEN's Uitgevers-Maatschappij, Amsterdam C., O.Z. Voorburgwal 115, telefoon 48695,
postrekening 39514.

INHOUD: Mededeelingen van het Secretariaat der Nederlandsche Chemische Vereeniging. — Contributie 1938. — Gereduceerde contributie. — Analystexamen 1e gedeelte, diploma A en B. — Bond voor Materialenkennis. — Aangeboden betrekkingen. — Prof. Dr. A. Smits en Dr. W. A. Burgers, In memoriam Dr. N. F. Moerman. — Symposium on Hydrophobic Colloids held in Utrecht on the 5th and 6th of November 1937, III. — Boekaankondigingen. — Chemische kringen. — Personalia, enz. — Ter bespreking ontvangen boeken. — Correspondentie, enz. — Gevraagde betrekkingen. — Vraag en aanbod. — Economische berichten.

MEDEDEELINGEN VAN HET SECRETARIAAT DER NEDERLANDSCHE CHEMISCHE VEREENIGING

(Willem Witsenplein 6, 's-Gravenhage, telefoon 774520, postrekening 7680).

Nieuwe leden.

De in het Chemisch Weekblad van 4 December 1937 onder 72—78 genoemde candidaat-leden zijn thans aangenomen als gewone of buitengewone leden.

VERBETERING.

De in het Chem. Weekblad van 29 Januari 1938 onder 109—112 genoemde *Candidaat-leden* waren *allen* voorgesteld door Dr. J. v. Alphen en drs. J. C. Freelink, beiden te Leiden.

* * *

Candidaat-leden:

115: Jansen (Th. J.), ap.. Rotterdam-C., Mathenesserlaan 162b, dir. v. h. filiaal Rotterdam der N.V. Kon. Pharm. Fabrieken v. h. Brocades, Stheeman & Pharmacia; voorgesteld door Dr. H. van Veldhuizen en Ir. A. C. van Wijk, beiden te Rotterdam.

116: Overeem (Mej. E. M. van), chem. cand., Leiden, Nieuwsteeg 2; voorgesteld door Dr. J. van Alphen en drs. J. G. Frielink, beiden te Leiden.

117: Bekk (Dr. Ing. J.), Amsterdam-Z., Amstelkade 167 I, leider v. h. lab. G. H. Bührmann, Papiergroothandel N.V.; voorgesteld door Ir. L. de Weerd te Overveen en Dr. T. v. d. Linden, den Haag.

118: Dippy (Dr. J. F. J.), Cardiff, Department of Chemistry, The Technical College; voorgesteld door Prof. Dr. S. C. J. Olivier te Wageningen en Dr. T. v. d. Linden, den Haag.

Veranderingen aan te brengen in de ledenlijst 1937.

Blz. 30: Bontenbal (Ir. J.), Bombay, Postbox 353, ing. b. d. Hindustan Vanaspati Mfg Co Ltd.
„ „ : Borst (Mej. Ir. C. de), den Haag, Trompstraat 95, ing. b. h. Centr. Norm. Bureau.
„ 31: Brester (Dr. A.), Voorburg, Hoekenburglaan 10.
„ 32: Broekman (Ir. H. M. van Mourik), Beverwijk, Zeestraat 253.
„ 52: Iterson (Ir. J. A. Roessingh van), Soengei Gerong, Palembang (N. O.-I.), c. o. Ned. Kol. Petr.-Mij.
„ 69: Oosten (drs. R. P. van), Groningen, N. Ebbingestraat 79a.
„ „ : Oosterhoff (drs. L. J.), Leiden, Zoeterwoudschesingel 104.
„ 79: Schrieke (Ir. O. B.), Klaten, Java (N. O.-I.), Stationsweg, ass. a/h. proefst. der Klatensche Cultuur-Mij.
„ „ : Schuit (drs. G. C. A.), Leiden, van 't Hoffstraat 20 B, scheik. b. d. B. P. M.
Blz. 86: Vegt (drs. J. van der), Ambt Delden (O.), Goorschestraat A 50a, scheik. b. d. N.V. Chem. fabr. „Servo".
„ 92: Werre (Dr. J. P.), Leiden, Lammenschansweg 20, scheik. b. d. B. P. M.
„ „ : West (Mej. Ir. E. van), den Haag, Zeestraat 73, flatgebouw Willemspark, flat 401.

Adresveranderingen, enz. van (candidaat-)leden, wier namen nog niet in de ledenlijst zijn opgenomen.

Blz. 47: Heilmann (drs. E. L.), Scheveningen, Leuvenschestraat 26.

* * *

De Secretaris is iederen Maandagmiddag van 1.30 tot 3 uur aan bovenstaand adres te spreken. Het Bureau is in den regel geopend iederen werkdag van 9—12 en van 1.30 tot 4.30 uur, des Woensdags en des Zaterdags van 9—12 uur.

Dr. T. VAN DER LINDEN,
den Haag, telefoon **721636** (na 6 u. n.m.).

Contributie 1938.

De aandacht wordt er op gevestigd, dat volgens art. 5 van het Huishoudelijk Reglement, de jaarlijksche contributies invorderbaar zijn van 1 Januari af.

Aan gewone leden, *die geen reductie op de contributie hebben aangevraagd*, aan buitengewone, geassocieerde en huisgenootleden wordt daarom verzocht, het door ieder verschuldigde bedrag, n.l.

a. *f* 15.— voor *gewone* leden in Nederland, N. O.- en W.-Indië;
b. 17.— „ „ „ „ het buitenland;
c. 10.— „ *buitengewone* leden;
d. 7.50 „ *geassocieerde* leden;
e. 5.— „ *huisgenoot*-leden,

in de gevallen *a*, *b*, *d* en *e* eventueel te vermeerderen met *f* 6.—, in het geval *c* met *f* 4.—, voor een *abonnement op het Receuil*, zoo spoedig mogelijk te doen overschrijven op postrekening 7680 der Ned. Chem. Vereeniging te 's-Gravenhage.

De Penningmeester roept de medewerking van alle leden in, om in het belang der Vereeniging te komen tot een vlotte inning van de verschillende contributies.

Gereduceerde contributie.

Krachtens besluit van de Algemeene Vergadering kan het Algemeen Bestuur de contributie voor 1938 van **gewone leden**, op hun verzoek, als volgt vaststellen:

a. voor hen, die op 1 Januari *ongehuwd* zijn:
bij een **totaal-inkomen** kleiner dan *f* 1500.— op . . . *f* 5.—
„ „ „ „ van *f* 1500.— tot beneden *f* 1800.— op . . . . „ 10.—

Onder *inkomen* wordt hierbij verstaan het zuivere inkomen naar den laatst bekenden aanslag in de Rijksinkomstenbelasting, behoudens sedert de vaststelling daarvan ingetreden belangrijke wijzigingen.

b. voor hen, die op 1 Januari *gehuwd* zijn:
bij een **totaal-gezins-inkomen** kleiner dan *f* 2000.— op *f* 5.—
„ „ „ „ van *f* 2000.— tot beneden *f* 3000.— op . . . . „ 10.—

Onder *gezinsinkomen* wordt hierbij verstaan het gezamenlijke inkomen van het lid, echtgenoot(e) en inwonende kinderen, die eigen inkomsten hebben.

De reductie moet *vóór 15 Februari a.s.* (door hen, die in den loop van het vereenigingsjaar als lid toetreden, binnen een maand nadat zij de kennisgeving van inschrijving hebben ontvangen) worden aangevraagd door middel van een formulier, dat op verzoek door het Secretariaat wordt toegezonden (OOK DOOR HEN, DIE REEDS IN EEN VORIG JAAR REDUCTIE OP DE CONTRIBUTIE GENOTEN). Het Algemeen Bestuur behoudt zich het recht voor, reductie te weigeren, indien deze niet op tijd is aangevraagd of indien de aanvrager — na daartoe te zijn uitgenoodigd — naar de meening van het Algemeen Bestuur niet voldoende aannemelijk maakt, dat de verstrekte gegevens juist zijn.

Een gereduceerde contributie van *f* 5.— moet worden voldaan binnen een maand, nadat de reductie is toegestaan, een gereduceerde contributie van *f* 10.— in ten hoogste 2 gelijke termijnen, waarvan de eene vervalt binnen een maand, nadat de reductie is toegestaan, de andere 3 maanden later.

Indien leden, aan wie reductie op de contributie is toegestaan, in den loop van het vereenigingsjaar in omstandigheden komen te verkeeren, waarin het betalen der normale contributie voor hen geen bezwaar meer oplevert, verwacht het Algemeen Bestuur, dat zij de betaalde contributie tot het normale bedrag zullen aanvullen.

De abonnementsprijs van het Recueil is voor alle gewone leden gelijk en bedraagt *f* 6.— per jaar. Dit bedrag moet in zijn geheel, tezamen met den eersten termijn der contributie, worden voldaan.

Analyst-examen 1e gedeelte Diploma A en B.

De oproep voor het op Vrijdag 18 Februari a.s. te houden schriftelijk examen in natuur- en scheikunde is op 1 Februari aan de candidaten gezonden.

Schiebroek,
Adrianalaan 163
(Telefoon 41250-
Rotterdam).

Dr. J. VAN DER LEE,
Secretaris van de Centrale Commissie
voor het Analyst-examen.

Bond voor Materialenkennis.

De Bond voor Materialenkennis organiseert dit jaar een cursus in Limburg in samenwerking met de Nederlandsche Vereeniging voor Laschtechniek (afd. Limburg). Prof. Dr. Ir. W. F. Brandsma heeft zich bereid verklaard dezen cursus te houden met als onderwerp: *„De materiaalkeuze bij de vervaardiging van machineonderdeelen en gereedschappen".*

De voordrachten zullen gehouden worden op vijf achtereenvolgende Vrijdagavonden, te beginnen op 11 Maart 1938. De eerste vijf bijeenkomsten zullen plaats hebben in het Beambtencasino Emma-Hendrik te Hoensbroek. Zij zullen precies om 20 uur aanvangen en eindigen om 21.45 uur met een daartusschen gelegen pauze van ongeveer 15 minuten.

Vrijdag 11 Maart 1938.

Inleiding. Enkele mechanische eigenschappen (trekvastheid, strekgrens, vloeigrens, rek en hardheid). Methoden om deze te bepalen. De versteviging door deformatie en de rekristallisatie. Giet-, wals- en perslegeeringen. Giet- en walstechnisch belangrijke eigenschappen. Eerste vormgeving door gieten of door plastisch vervormen. Bewerkbaarheid met snijdend gereedschap. Compromis tusschen eischen van het eindproduct en eischen van het productieproces. Algemeene regels voor een juiste metaalkeuze.

Vrijdag 18 Maart 1938.

Warmtebehandelingen. De structuur van de metalen. Deformatie en versteviging. Het veredelen van aluminiumlegeeringen. Het harden van staal. Theorie van Maurer. Beteekenis van het ontlaten na het harden. Invloed van legeeringselementen. Water-, olie- en luchthardend staal. Doorharden van staal. Cementeeren en veredelen. Hardingsovens en zoutbaden. Vervormingen bij harden en gloeien. Overzicht van de warmtebehandelingen.

Vrijdag 25 Maart 1938.

Gietlegeeringen. Mechanische eigenschappen. Gietijzer (perlitisch-, smeedbaar-, gelegeerd). Gietstaal. Invloed van legeeringselementen. Gietmessing, -brons, -aluminium, witmetaal. Bewerkbaarheid. Schema voor de keuze van gietlegeeringen.

Vrijdag 1 April 1938.

Wals- en smeedlegeeringen. Mechanische eigenschappen. Toelaatbare spanningen bij statische en dynamische belasting. Nauwkeurigheid en uiterlijk van het bewerkte oppervlak. Vloeistaal, gelegeerd- en veredeld staal. Bewerkbaarheid bij plastische vervorming. Bewerkbaarheid bij snijdende bewerking. De normalisatie van constructiestalen. Roestvrij staal. Niet-ijzermetalen. Schema voor keuze van gewalst materiaal voor constructies en machines.

Vrijdag 8 April 1938.

Staal voor gereedschappen. Ongelegeerd en gelegeerd staal. Invloed van chroom, wolfraam e.a. Het smeden en harden van ledeburitisch staal. Slag of stootgereedschap. Snijgereedschap, stempelstaal en snelstaal. Analyse van de eischen voor gereedschapstaal. Snijsnelheid bij verschillende bewerkingen. Wanneer gebruikt men snijmetalen. Schema voor de metaal-keuze voor gereedschappen.

Zaterdagmiddag 9 April 1938, 14 uur.

Demonstraties in het Metallographisch Laboratorium der Technische Hoogeschool, Nieuwelaan 76, Delft.

Mechanisch onderzoek: Trekproef voor koper, vloeistof en gietijzer. Martens spiegelapparaat. Buigproef voor gietijzer. Hardheidmeters. Hardheid van gietijzer, staal en messing. Doorhardend en nietdoorhardend staal. Gecementeerd en gehard staal. Vermoeidheidsproeven.

Microscopisch onderzoek: Gegloeid en gehard staal. Gietijzer, gelegeerd staal, snelstaal, messing, brons, witmetaal.

Voor degenen, die niet in de gelegenheid zijn voor dit doel naar Delft te komen, zullen enkele materiaalbeproevingsmachines en preparaten van metalen op een nader te bepalen dag in het Centraal Proefstation en Laboratorium van de Staatsmijnen getoond kunnen worden.

Aanmelding tot deelneming kan geschieden bij het secretariaat van den Bond voor Materialenkennis, Da Costakade 104, Postbox 6005, Amsterdam-W., tot en met Zaterdag 5 Maart 1938, of wel bij den heer F. Groenewegen, secretaris der Nederl. Vereeniging voor Laschtechniek, afd. Limburg, Dr. Clemens Meulemansstraat 18a, Heerlen. Vóór dien tijd moet ook het cursusgeld voldaan zijn door storting op de postgirorekening van den penningmeester van den Bond voor Materialenkennis, *No. 209046 te Amsterdam.* Indien de aanmelding op deze wijze is gecompleteerd, wordt de *persoonlijke* deelnemerskaart toegezonden.

Het cursusgeld voor den geheelen cursus bedraagt *f* 15.— per persoon. Dit wordt verlaagd tot *f* 10.— per persoon voor hen, die — inschrijvende voor zichzelf of voor hun employé's — lid of donateur zijn van één der volgende vereenigingen: Bond voor Materialenkennis, Koninklijk Instituut van Ingenieurs, Nederlandsche Chemische Vereeniging, Nederlandsche Vereeniging van Gieterij-Technici, Nederlandsche Vereeniging voor Laschtechniek, Vereeniging van Delftsche Ingenieurs, Vereeniging van Technici op Scheepvaartgebied.

J. L. BIENFAIT, secretaris.

Aangeboden betrekkingen, werk, subsidies, enz. **)

Assistent-redacteur. Met ingang van 1 Maart a.s. is de betrekking te vervullen van assistent op het Redactiebureau van Chem. Weekblad en Rec. trav. chim. Salaris *f* 1400.— tot *f* 1800.— 's jaars. In aanmerking komen doctoren en doctorandi in de chemie en scheikundig ingenieurs. *Schriftelijke* aanmelding bij het Secretariaat der Nederl. Chem. Vereeniging, Willem Witsenplein 6, 's-Gravenhage, tot *uiterlijk* 15 Febr. a.s.

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Aan het Rijkszuivelstation te Leiden is, met ingang van 1 Mei 1938, te vervullen de betrekking van *scheikundige,* bij voorkeur met ervaring op het gebied van zuivelbacteriologie. Salarisgrenzen *f* 2160.— tot *f* 5400.—. Zie verder de adv. in Nr. 6.

⁂

De N.V. Polak & Schwarz's Essencefabrieken te Hilversum zoekt voor tijdelijk een scheikundige, bij voorkeur op de hoogte van het organisch-analytisch onderzoek van plantaardige producten.

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Zie vervolg op blz. 139.

**) *Men raadplege ook steeds de advertenties.*

54 : 92 M

IN MEMORIAM DR. N. F. MOERMAN.

Het is zoo ontzaglijk moeilijk zich te realiseeren, dat die sympathieke, temperamentvolle en uiterst begaafde jongeman Nicolaas Frederik Moerman[1] plotseling van ons is weggenomen. Dit is voor zijn familie, zijn vrienden en voor mij een zware slag. Als leerling der Amsterdamsche Universiteit maakte Moerman van den beginne af een buitengewoon gunstigen indruk op zijn leermeesters en de verwachting van hen, die hem het best konden beoordeelen, was dan ook, dat er iets bijzonders uit hem groeien zou. Dit is geheel bewaarheid geworden en gedurende den mooien tijd, dat hij mijn assistent en medewerker was, heb ik met de grootste belangstelling en voldoening zijn snellen groei tot een zelfstandig wetenschappelijk onderzoeker waargenomen. Zijn helder inzicht en zijn groot bevattingsvermogen maakten het al spoedig tot een genot met hem wetenschappelijke problemen te bespreken.

Zijn levendige fantasie en intuïtie maakten, dat hij het probleem direct juist aanvoelde en doorzag. Hij bezat reeds als 3de jaars candidaat een goeden kijk op verschillende gebieden der chemie en toch las hij in dien tijd niet veel. De oplossing van dit raadsel lag daarin, dat hij een wetenschappelijk werk slechts korten tijd had in te zien om de quintessens eruit op te diepen. Hij kon het werk van anderen scherp en op humoristische wijze critiseeren en met zijn warm temperament, soms wel wat al te scherp, maar zijn oordeel was bijna altijd volkomen juist.

Het spreekt wel van zelf, dat de studie van zoo'n begaafd en enthousiast student buitengewoon voorspoedig is geweest. Hij deed dan ook reeds in Juni 1936 op 22-jarigen leeftijd doctoraal examen, met physische chemie als hoofdrichting, en verwierf daarbij het praedicaat „cum laude". Hij was intusschen reeds aan zijn dissertatie-onderwerp begonnen en promoveerde 17 Maart 1937, dus 9 maanden later, op 23-jarigen leeftijd, op een dissertatie getiteld: *„Het physisch-chemisch gedrag van de complexe stof* SO_3*"*. Bij deze gelegenheid werd hem op grond van zijn zéér verdienstelijk werk eveneens het praedicaat „cum laude" toegekend.

Hoe gaarne had ik hem aan mijn laboratorium verbonden gehouden. Waren de tijden gunstiger geweest, dan zou ik daarvoor zeker moeite hebben gedaan, maar onder de gegeven omstandigheden was daarvan niets te verwachten.

Moerman was de kostwinner voor zijn familie en moest, om een beter gesalarieerde positie te verkrijgen, zijn assistentschap helaas prijs geven. Voor zijn promotie had ik reeds met collega Holst over Moerman gesproken en het bleek toen, dat hij hem gaarne aan de wetenschappelijke natuurkundige afdeeling van het laboratorium der Philips-fabrieken wilde verbinden. Een paar uur voor de promotie ontving Moerman telegrafisch de mededeeling, dat hij was aangesteld. Een fijngevoelde daad, die den dag van zijn promotie tot een dubbelen feestdag maakte. Bij die gelegenheid zei ik hem o.a., dat het belangrijkste waarop ik wijzen kon wel dit was, dat hij zich tot een uitnemend zelfstandig wetenschappelijk onderzoeker had ontwikkeld en dat het geheel overbodig was er hem op te wijzen, dat hij, met zijn zéér bijzonderen aanleg, verplicht was zich aan de wetenschap te blijven wijden; hij zou dat natuurlijk doen, zoo merkte ik op, omdat hij eenvoudig niet anders zou kunnen en op deze overtuiging was mijn vertrouwen in zijn toekomst gevestigd. Alles verliep inderdaad zoo gunstig als men slechts wenschen kon, want iemand van de capaciteiten van Moerman had nergens beter op zijn plaats kunnen zijn dan op het wetenschappelijk laboratorium der Philipsfabrieken. Het zou dan ook zeer voorspoedig met hem gegaan zijn, wanneer zijn leven niet plotseling was afgebroken, want hoewel hij slechts 9 maanden in zijn nieuwe betrekking heeft mogen werken, heeft men hem in dien korten tijd als physico-chemicus en als mensch in hooge mate leeren waardeeren.

Wat heeft deze jongeman, die slechts den 24-jarigen leeftijd bereikte, tot stand gebracht? Ten eerste dan zijn mooie dissertatie, die als een voortzetting van de dissertatie van Schoenmaker (1926) is te beschouwen. Het onderzoek moest in verschillende richtingen worden voortgezet en ik moest daartoe iemand trachten te vinden met die capaciteiten, die voor zoo'n subtiel en moeilijk werk worden vereischt. Het was wel een bijzonder gunstige omstandigheid, dat ik mijn assistent Moerman dit onderzoek kon opdragen. Zelden zag ik iemand met zóóveel enthousiasme een probleem aanvatten en het was mede aan zijn helder inzicht, zijn initiatief en zijn experimenteele vaardigheid te danken, dat er spoedig een dissertatie kon verschijnen, die volledige inlichtingen omtrent het bijzondere gedrag van de stof SO_3 gaf. Er werd gevonden, dat wanneer de dampspanning van een verstoorden toestand als functie van den tijd werd nagegaan en ten slotte de dampspanning van den innerlijken evenwichtstoestand was bereikt, toch nog slechts een zéér klein deel innerlijk in evenwicht was gekomen. Dit werd bewezen door bepaling van de oploswarmte in geconc. H_2SO_4. De oploswarmte toonde tevens aan, dat de verstoorde toestanden met abnormaal lage dampspanning een aanmerkelijk grootere energie bezitten dan de toestand in innerlijk evenwicht. Dat bestraling met Röntgenlicht de instelling van het innerlijk evenwicht in den vasten toestand versnelt, was reeds vroeger aangetoond, maar door bepaling van de oploswarmte na voldoend lange bestraling kon nu worden bewezen, dat het Röntgenlicht de geheele massa in innerlijk evenwicht brengt. Verder bleek, dat de innerlijke transformatie die hierbij plaats grijpt, in afwijking van de thermische transformatie, een reactie van de nulde orde is. Deze onderzoekingen werden aangevuld met de studie van het *Raman-effect* en de meting van de *diëlectriciteitskonstante*, met het doel, den aard en de structuur der pseudokomponenten te leeren kennen. Gerding, Nijveld en Muller bestudeerden den dampen vloeistoftoestand, terwijl aan Moerman de vaste toestanden werden toevertrouwd. Voor zoover de studie van het *Raman-effect* in staat was de resultaten van het voorafgegane thermodynamische onderzoek te toetsen, werd er volkomen bevestiging gevonden. Verder is vast komen te staan, dat er naast enkelvoudige moleculen SO_3, polymeren voor-

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[1] Geboren 4 Dec. 1913, overleden 20 Jan. 1938.

komen en dat het eenvoudigste polymeer daaronder $(SO_3)_3$ is, dat een ringstructuur bezit.

Dit resultaat maakte een diepen indruk op Moerman en met ijver ging hij na, bij welke stoffen vermoedelijk ook zoo'n ringstructuur zal voorkomen. Voor het feit, dat de Röntgenanalyse deze nog niet bij organische stoffen had ontdekt, geeft hij op de laatste bladzijde van zijn dissertatie een juiste verklaring. Hij zegt daar het volgende: „Het betrekkelijk geringe succes, dat de Röntgenanalyse tot nog toe aan organische stoffen gebracht heeft moet m.i. voor een deel daaraan toegeschreven worden, dat men niet genoeg rekening heeft gehouden met het feit, dat vóór men aan de physische beinvloeding (plaatsing van moleculen in het rooster) kan gaan denken, men eerst moet weten welke molecuulsoorten in de vaste stof te verwachten zijn. Een merkwaardig voorbeeld hiervan levert het onderzoek van het acetamide.

De auteurs hebben hier de oplossing voor het grijpen. Het vasthouden aan de plaatsingsmogelijkheid van de enkelmoleculen maakt echter, dat zij bij de bepaling van de ruimte-groep zijn blijven steken. Wanneer men bedenkt, dat vloeibaar acetamide sterk geassocieerd is en dat dus de kans, dat het rooster in hoofdzaak uit polymere moleculen opgebouwd is, zeer groot is, ziet men onmiddellijk hoe de structuur uit $(CH_3\,CONH_2)_3$-moleculen opgebouwd is. Hieruit volgt ook, dat de polymeren werkelijk nieuw ontstane chemische individuen zijn, wier chemische eigenschappen b.v. ook geheel anders kunnen zijn als die van de moleculen, waaruit zij opgebouwd zijn."

Op dezen zeer juisten gedachtengang voortbouwend heeft hij zich, grootendeels in samenwerking met Wiebenga, in den laatsten tijd door middel van Röntgenanalyse met andere organische ringsystemen bezig gehouden, zooals trioxymethyleen, trithiomethyleen en cyanuurzuur. Verder onderzochten zij de cubische vormen van hexachlooraethaan, hexamethylaethaan en dicyaanaethaan in verband met de rotatie der moleculen in den vasten toestand. Het meerendeel van deze onderzoekingen is nog niet gepubliceerd. Wat hier zeker niet vergeten mag worden is een publicatie van Moerman en Muller, getiteld *„Zur Frage der Umwandlungen höherer Ordnung"*[1]). Deze uitnemende verhandeling, die van helder inzicht getuigt, zal nog vele jaren voor menigeen een ernstige waarschuwing zijn om zich niet lichtvaardig aan allerlei speculaties over te geven.

Zoo was dat korte leven van Moerman dus een uiterst vruchtbaar leven, dat de mooiste verwachtingen voor de toekomst deed koesteren.

Ik was niet in staat bij het graf van Moerman te spreken en daarom heb ik op deze manier een en ander gezegd, maar ik moet daar nog iets aan toevoegen. Moerman was mij in hooge mate sympathiek, niet alleen om zijn chemische capaciteiten, maar ook om zijn eigenschappen als mensch. Hij behoorde juist tot dat type, dat ik boven alles waardeer; hij was zeer open, rond, eerlijk, spontaan en volkomen betrouwbaar. Hij dacht hardop, kende geen omwegen, maar ging steeds recht op zijn doel af. Hij was een persoonlijkheid met een warmvoelend hart; zijn handdruk zei alles! Hij was een groot vriend van de natuur en trad gaarne als leider bij de N.J.N. „de Nederlandsche Jeugdbond voor Natuurvrienden" op. Hij was artistiek aangelegd, hetgeen ook in zijn behandeling van wetenschappelijke problemen tot uiting kwam. Hij teekende en schilderde zeer verdienstelijk en ik waardeer het zéér een aardig schilderstukje van hem te bezitten, dat hij mij bij zijn vertrek naar Eindhoven ten geschenke gaf.

Het leed, dat door zijn dood aan zijn ouders en zuster werd opgelegd, is bijna niet te dragen. Het is alleen de herinnering aan het vele, waarmede hij het leven van hen in die weinige jaren heeft verrijkt, die eenigermate den last kan verlichten.

Moge dit zoo zijn!

A. SMITS.

Amsterdam, Jan. 1938.

Moerman is slechts korten tijd in ons midden op het laboratorium geweest. Ik zelf had niet direct met zijn werk te maken. Maar omdat de röntgeninstallatie voor kristalonderzoek door mij beheerd wordt, kwam ik al vanaf den eersten tijd, dat hij op het laboratorium werkte, dikwijls met hem in aanraking, zij het, dat hij opnamen noodig had van praeparaten, die met zijn werk hier samenhingen, zij het, dat hij nog enkele foto's wilde maken ter aanvulling van het door hem in Amsterdam begonnen en hier in zijn vrijen tijd zoo succesvol voortgezette werk over de kristalstructuur van bepaalde organische verbindingen.

Graag zou ik hier tot uiting brengen, hoe zeer mij daarbij steeds, naast de buitengewone grondigheid van zijn kennis, de bescheidenheid in zijn optreden en de prettige wijze, waarop hij omging met allen, waarmee hij in aanraking kwam, getroffen heeft. De opgewektheid en de ongekunstelde voldoening waarmee hij van een gevonden uitkomst vertellen kon, vormen een herinnering voor altijd.

Bij een zoo ontzettenden slag, als dit verlies voor zijn Ouders in het bijzonder moet beteekenen, durft men niet van troost spreken. Het eenige, dat wij voor hen kunnen doen, is hun zoon in onze gedachten houden, zooals wij hem gekend hebben, met zijn opgewekte gezicht en de natuurlijkheid van zijn geheele persoon.

Eindhoven, 20 Januari 1938.

W. G. BURGERS.

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[1]) Physik Z. 38, 298 (1937).

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SYMPOSIUM ON HYDROPHOBIC COLLOIDS HELD IN UTRECHT ON THE 5th AND 6th OF NOVEMBER 1937.

III.

Dr. Voet presented the following paper *).

Lyotropic effects in lyophobic systems

by

Andr. Voet (Amsterdam).

1. It is a wel known fact in colloid chemistry, that the valency rule of Schulze is only an approximate expression of the flocculation values of hydrophobic colloids. When we consider the flocculation of negative sols by univalent ions, we notice a clearly expressed lyotropic influence.

Flocculating several negative sols with alkali chlorides, N. Papadà[1]) observed the order:

$$Cs \rangle Rb \rangle K \rangle Na \rangle Li.$$

where Cs shows the strongest and Li the weakest flocculation power. P. Tuorila[2]) showed that this sequence holds true in the flocculation of gold and paraffin sols as well as with quartz, clay and permutit suspensions with alkali chlorides.

Comparing this order with the sequence of ionic radii, we notice that the larger ion always shows the greater flocculation power. When flocculating positive sols by electrolytes, a lyotropic influence is also observed. Flocculating a ferric hydroxyde sol, Weiser en Middleton[3]) observed the order:

$$Cl' \rangle ClO'_3 \rangle NO'_3 \rangle Br' \rangle I'$$

where Cl′ shows the strongest and I′ the weakest flocculation power. The same order is generally found with flocculation experiments with positive sols. When carrying out experiments with an aluminium hydroxide sol, Robinson[4]) observed the order

$$Cl' \rangle Br' \rangle I' \rangle CNS'.$$

Comparing this order with the sequence of ionic radii, we observe, that there the smallest ion shows the greatest flocculation power. These positive sols are without doubt hydrated to some extent and form an intermediate case between hydrophilic and hydrophobic colloids. Flocculating a truly hydrophobic sol, (a positive gold sol prepared by reversing the charge of an ordinary gold sol), the following sequence of flocculation power of potassium salts was found by Voet en Balkema[5]):

$$Cl' \langle Br' \langle I' \langle CNS'$$

where the largest ion shows the highest flocculation power. From these experiments we conclude, that in flocculation of hydrophobic sols with ions of the same valency, the larger ions have the greater effect. As is known, the reverse is true, of the flocculation of sols of proteins, agar, starch, etc. The higher flocculation power of smaller ions with hydrophilic colloids may be explained by their high dehydrating effect.

2. The lyotropic sequence of ionic action is found in many physical chemical processes. Recently a new method, originated by Bruins[6]) and developed by others[7]), has enabled us to express quantitatively the lyotropic activities of the different ions in various processes. Along the same lines it is possible to show from experiments that different phenomena, such as salting out, swelling, gelation and solation of lyophilic colloids, viscosity of salt solutions, influence of salts on rate of reactions, ionic exchange, heat of hydration and potential of ionization are closely related to the energy of the ionic electric field. Mathematically this relationship is known as a projective one.

In studying the litterature on the flocculating influence of salts on lyophobic colloids, it was found, that nearly all known investigations are unsuited for quantitative treatment since very undefinite criteria such as first turbidity, flocks formed in a certain period of time, etc. were generally used. It has only been worth while to recalculate results of investigations in which the progressing flocculation was observed by counting the decrease in the number of particles. From the very accurate and extensive experiments of Tuorila[2]), it was possible to show that the influence of different ions on the flocculation of a hydrophobic colloid is an example of a simple lyotropic effect.

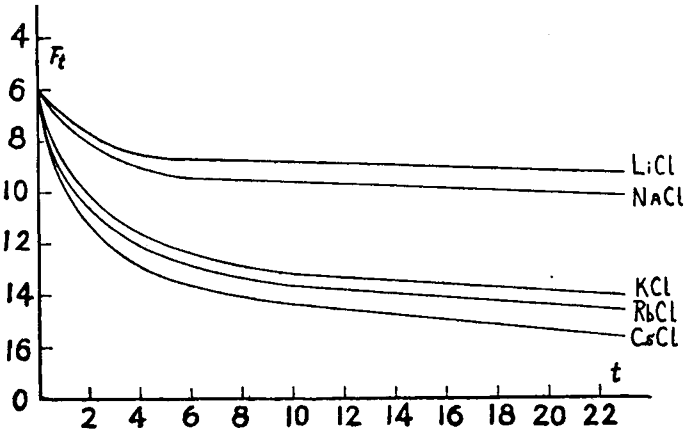

Fig. 1.

It has been pointed out, that the curves of fig. 1, showing the decrease with time of the number of particles of a gold sol, flocculated with alkali chlorides, are equilateral hyperboles, which are in projective relationship[8]).

Since, as has already been pointed out, the same numerical relations occur with different lyotropic

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*) This paper, which was read already on the day before (for certain reasons of organisation) is printed here, because this order of subsequence is more logical.

[1]) N. Papadà, Kolloid-Z. 9, 137 (1911).

[2]) P. Tuorila, Kolloid-Beihefte 22, 298 (1926).

[3]) H. Weiser & E. A. Middleton, J. Phys. Chem. 30, 600 (1924).

[4]) C. Robinson, Thesis 1929 Utrecht.

[5]) Andr. Voet en F. Balkema, Rec. trav. chim. 52, 371 (1933).

[6]) E. M. Bruins, Proc. Akad. Wetenschappen Amsterdam 35, 107 (1932).

[7]) Comprehensive Reports: E. H. Buchner, Kolloid-Z. 75, 1 (1936); J. H. C. Merckel, Thesis Amsterdam 1934; Andr. Voet, Chem. Rev. 20, 169 (1937).

[8]) E. H. Buchner, Andr. Voet en E. M. Bruins, Proc. Akad. Wetenschappen Amsterdam 35, 596 (1932); Andr. Voet, Kolloid-Z. 78, 201 (1937).

phenomena, it is easy to show a close correlation between the flocculation power of the ions and the energy of their electric fields.

3. Concerning the cause of the sequence of ionic flocculation power, different views were expressed by different authors.

a. Wiegner⁹) explained the lyotropic order by pointing out, that the "effective" volume of the smaller ions is really the larger because of their great hydration. Consequently the distances between centres of oppositely charged ions in the double layer should be larger with more hydrated ions which therefore have a smaller electrokinetic potential. This conception correlates the lyotropy with interaction with the medium, which is, as we have seen, correct. However, since we now have a better insight into the mechanism of the double layer, it is clear that, especially in the more dilute solutions where lyotropic effects equally exists, no steric hindrance ever can explain these effects. Therefore Wiegner's explanations are not completely correct.

b. Different authors¹⁰) explain the lyotropic effects by assuming specific forces, generally due to the ionic polarisability, between the ions and the charged walls of the colloid particle, neglecting completely the ionic interaction with the solvent. This conception may lead to ionic exchange in the diffuse double layer or even to adsorption of the oppositely charged ions. The latter case corresponds to a flocculation by direct decrease of the particle charge, as was required by Freundlich's old theory of flocculation.

Many objections to these views may be raised especially from the experimental standpoint.

I. The quantitative sequence of ionic polarisability (also per unit volume) is distinctly different from the flocculation effects, since the first mentioned ionic property does not at all obeye the lyotropic projective relationship, whereas the latter property obeys it perfectly. This may be observed directly from the small differences in flocculation power between the potassium and rubidium ions, corresponding to their slightly different energy of hydration, whilst the differences in polarisability are much more pronounced.

II. From the theoretical standpoint, there are many possibilities for alterations in the double layer when the concentration of the electrolytes in bulk is changed¹¹). We must however keep the experimental facts clearly in view. If the electrokinetic potential of a glass capillary is plotted against the electrolyte concentration, an increase followed by a decrease is observed¹²) (fig. 2), while the density of charge on the wall increases at first but afterwards tends towards a constant value which is reached at a concentration of about 2.10^{-6} n¹³) (fig. 3).

The same effect is found with particles, such as graphite and collodion¹⁴), where a constant particle

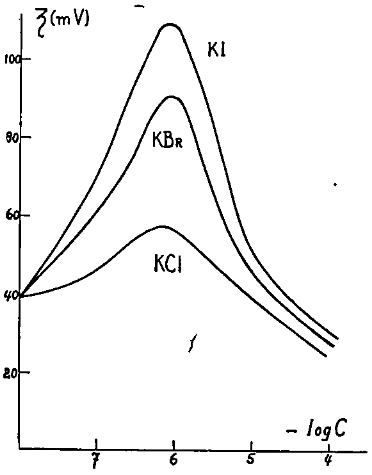

Fig. 2.

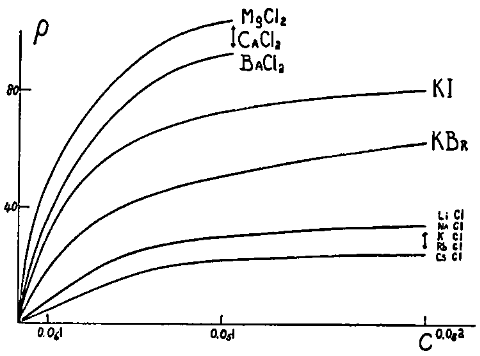

Fig. 3.

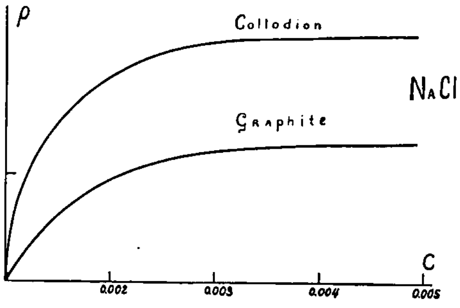

Fig. 4.

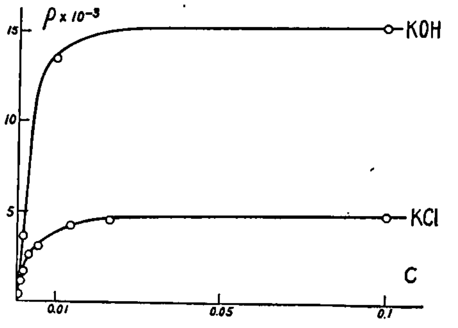

Fig. 5.

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[9] G. Wiegner, Kolloid-Z. **36 A**, 343 (1925).

[10] E. J. W. Verwey, Chem. Rev. **16**, 363 (1935).

[11] E. J. W. Verwey, This Symposion, page 70.

[12] N. Furutani et al, Japan J. Gastroenterol **2**, 148 (1930).

[13] H. A. Abramson, Electrokinetic Phenomena (New York, 1934), calculated from the data of Furutani et al, l.c.; The density of charge has been corrected for its value in destilled water; L. W. Jansen (thesis Utrecht 1934) obtained quite analogous results, upon recalculating the data by H. R. Kruyt en P. C. v. d. Willigen, Kolloid-Z. **45**, 307 (1933).

[14] H. A. Abramson en H. Müller, Cold Spring Harbor Symposium **1**, 32 (1933).

charge is observed from an electrolyte concentration of about 0.003 N and higher (fig. 4). Experiments with oil droplets show, that this constancy of charge is maintained at concentrations as high as 0.1 n (fig. 5). From these experiments we conclude that, at the flocculating electrolyte concentration for lyophobic colloids, which for uni-univalent electrolytes lies in the range from 0.01—0.1 n no change generally occurs in the particle charge.

This conclusion is in complete accordance with the recalculations of Freundlich & Zeh's flocculation experiments on the As_2S_3 sol by H. Müller[16]). In this case the author showed that the decrease of the ζ-potential is accompanied by a constant density of the particle charge, notwithstanding the presence of highly charged ions. As the initial electrolyte concentration is already at the maximum ζ-potential and density of charge, it is clear that any increase of electrolyte concentration may cause a decrease of the potential, due to concentration of the double layer, but it does not influence the density of charge of the particle, corresponding to figures 2 and 3, started at the concentration of the maximum electrokinetic potential. Since lyotropic effects occur under these circumstances, any theory based on a change of the particle charge must be incorrect.

III. It may be shown, that the lyotropic sequence occurs equally in systems, where an exchange of counter ions is excluded. Tuorila[17]) prepared different gold sols by reduction of dilute solutions of $HAuCl_4$ with formalin as well as with hydrogen peroxyde, each time in the presence of one of the different carbonates of the alkali metals. These sols, which were prepared under absolutely similar conditions showed exactly the same flocculation value towards NaCl, $BaCl_2$ and $La(NO_3)_3$ and might consequently be considered as exactly equivalent in stability[18]). Moreover, owing their method of preparation the counter ions of each sol were formed by one of the different alkali metal ions.

In the flocculation of a Li gold sol with different alkali chlorides, the usual lyotropic order was observed, the same was true in the flocculation of a K gold sol. If the lyotropic series were dependent upon ionic exchange, the flocculation values for LiCl, NaCl and KCl would be the same, as in these cases no ionic exchange could occur, since the K ion, which is the counter ion in the K gold-sol, exhibits the highest power of exchange.

When of four exactly equivalent gold sols, the Li gold sol was flocculated with LiCl, the Na gold sol with NaCl, the K gold sol with KCl and the Cs gold sol with CsCl, the lyotropic order was again observed quantitatively, notwithstanding the fact that in these cases the ions in the main body of the solution were exactly the same as the counter ions, and consequently no ionic exchange could ever take place.

Therefore ionic exchange cannot be the cause of the lyotropic order of the ions in flocculation experiments with hydrophobic colloids.

4. The present form of the theory of the diffuse double layer renounces the individuality of equally charged counter ions[19]).

The ionic partition is calculated as a result of the competition of electrical forces from the charged wall and the Brownian movement. According to the Boltzmann theorem, it is generally accepted that the following expression holds:

$$n_1 = n_0 \, e^{-\frac{z\varepsilon\varphi}{kT}} .$$

(n_1 is the number of ions per unit volume in a point with the average potential φ, n_0 is their number where $\varphi = 0$, $z\varepsilon$ is the ionic charge, k the Boltzmann constant and T the absolute temperature).

This expression may hold in a vacuum[20]), but is certainly incorrect in water, due to the different energies of interaction of the ions with the medium.

This free energy of hydration, which is entirely an electric effect, is proportional to the square of the charge and to the reciprocal ionic radius[21]).

It is generally accepted that the water dipoles around an ion are bound in the ionic electric field. The free energy of hydration of the ions is found in the difference of energy between the "orientated" or "bound" state of the water dipoles and the state of random distribution. To bring the ion in the vicinity of the double layer, where many molecules are already physically bound by the electric forces from the wall and from the accumulated ions, an extra amount of energy is necessary. This energy, which may only be supplied by the attractive forces from the wall, is due to the competition for the molecules of the solvent, and increases with increasing interaction with the medium. Consequently, with equally charged ions, where the forces from the wall are equal, the smaller ions encounter the higher energy barrier due to their larger energy of hydration.

Thus it is clear that the smaller ions have less tendency to move towards the wall.

This different behaviour must be introduced in the partition function, which may be written in the form

$$n_1 = n_0 \, e^{\frac{\varepsilon\varphi - f\left(\frac{z^2\varepsilon^2}{r}\right)}{kT}}$$

(r is the ionic radius and $f\left(\frac{z^2\varepsilon^2}{r}\right)$ is an unknown function of $\left(\frac{z^2\varepsilon^2}{r}\right)$ which shows that the ionic partition is effected by the competition of electric forces from the charged wall, counteracted by interaction with the medium and the Brownian movement of the ions. Further calculations on the basis of this function, which may easily be carried out in the usual way, show that the average thickness of the double layer is now dependent upon the radii of the counter

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[15]) P. Tuorila, l.c., recalculated by H. A. Abramson, l.c.

[16]) H. Müller, Kolloid-Beihefte **26**, 257 (1928).

[17]) P. Tuorila, l.c.

[18]) Tuorila reported however, that only the Cs-gold sol was slightly less stable.

[19]) The so called „radius" effect refers only to the central particle. Stern (Z. Electrochem. **30**, 508 (1924) introduces „adsorption potentials", which are unsuited to numerical treatment and in the authors opinion incorrect.

[20]) We shall not discuss here Hartley's criticism (Trans. Faraday Soc. 1935, General discussion on colloidal electrolytes) of the validity of the ionic partition on the basis of a Boltzmann function.

[21]) Discussion: Andr. Voet, Trans. Faraday Soc. **32**, 1301 (1936).

ions. In the same concentration the larger ions will cause the smaller average thickness, since they meet with fewer energy obstacles in moving towards the charged wall than the smaller ions. Consequently, with the larger ions of the same charge, which cause a greater decrease in the thickness of the double layer, the electrokinetic potential will be more decreased then with smaller ions. Therefore the former have a higher flocculation power than the latter.

In this way it is possible to explain the lyotropic order in flocculation experiments with lyophobic sols, without special assumptions, while the close connection with the energies of hydration, which was found by analysis of the experiments, is clearly indicated.

Summary.

1e. With purely hydrophobic colloids, those members of a group of equally charged ions, which have the smallest energy of hydration always have the highest flocculation power.

2e. Analysis of flocculation experiments show a quantitative connection between flocculation power and energy of hydration of the ions.

3e. Since the lyotropic order occurs equally in flocculation experiments where variation of charge as well as exchange of counter ions has been excluded, it is certain that the lyotropic sequence is not caused by these phenomena.

4e. The lyotropic order may be explained by the difference in decrease of the double layer caused by equally charged ions of different radius, due to their different energy of interaction with the medium.

Discussion.

Dr. Verwey readily agrees that the hydration of the ions plays an important part in the work needed to bring it from the solution to a point near the surface of the particle. However, the introduction of this hydration energy into the Debije-Hückel equations is not fundamentally different from Stern's conception, where, in addition to the electrical energy, each ion possesses an adsorption potential in the adhering layer. Stern's picture is probably more schematical and therefore simpler.

Dr. Voet answers: In my opinion, Dr. Verwey is essentially wrong in his conception about Stern's views. Quoting from the original publication (Electrochem. **30**, 508 (1924)) we find:

„....Die Zahl der adsorbierten Ionen sind nach „dem Boltzmannschen Satz bestimmt durch die Arbeit

$$\varphi = \varphi_{+} + e\,\psi \quad \text{resp.} \quad \varphi = \varphi_{-} - e\,\psi$$

„die nötig ist um ein positives, resp. negatives Ion „an die Grenzfläche heranzubringen. Dabei ist φ_{+} „resp. φ_{-} das gewöhnliche von den Molekularkraften „herrührende specifische Adsorptionspotential, das „für $\psi = 0$ allein vorhanden ist. Wir nemen „idealisierend an, dass φ_{-} und φ_{+} für die erste der „Metalloberfläche anliegende Molecularschicht von „Nul verschieden sind."

From this we learn that, according to Stern, the adsorption potential is independent of the ionic charge, while this is certainly not true of the energy of hydration. Furthermore Stern points out that the adsorption potential is independent of the charge of the wall.

According to this, Stern's adsorption potential is not at alle "schematical" but provided with distinct properties which fit very well in Dr. Verwey's picture of ionic polarisability, but are incompatable with my conceptions. I pointed out that the difference in tendency of equally charged ions to move towards the double layer, depends very much upon the wall charge. Furthermore this effect naturally acts at greater than molecular distances. Finally, any effect from any very short range force, as mentioned by Stern, would bring about ionic exchange or change in particle charge, whilst lyotropy exists equally well without these phenomena.

This makes it clear that there is a great difference between Stern's conception, used incorrectly to supply the cause of lyotropy and my views, where a quite different phenomenon, the interaction with the medium, is indicated as the cause of lyotropy.

Prof. Kruyt remarks: From all the rectilinear relations you mentioned, you choose deliberately that for the hydration as fundamental. That may seem arbitrary, but I can agree with you perfectly. On the other hand I should like to ask whether there is much difference between your explanation and that given by Robinson and me? We too emphasized the orientation of the water dipoles around the ion, and especially the large energy needed to bring dipoles, oriented in one sense, into a field with inversely oriented dipoles.

Dr. Voet replies: The only similarity, which I could find between Robinson's views as published in his thesis and mine are that we both consider the interaction with the medium as the cause of lyotropy in flocculation experiments with hydrophobic colloids. On the other hand, Robinson introduces the misleading idea of "favourable" and "unfavourable" orientation of dipoles. It is clear, that between two charged ions there is always competition about the water. If they are equally charged, the water between both ions is inversely orientated, which Robinson calls "unfavourable". If they are oppositely charged, they try to orientate the water with a quite different angle and consequently do not cooperate. The only "favourable" case would be the one possible water molecule, orientated in the line, connecting both centres of the ions. This is an exceptional case, owing the many possible places for the limited number of three dimensional orientated water molecules.

Furthermore, Robinson explains the lyotropic effect by assuming artificial hydration of a hydrophobic particle by adsorption of hydrated ions, which should give a certain stability to the particle after the decrease of the electrokinetic potential. Apart from impossibility of preferential adsorption of hydrated ions, this picture only fits in Freundlich's abandonned theory of flocculation. Since I showed that lyotropy exists equally under conditions where no change of particle charge or ionic exchange occurs, Robinson's views are unacceptable.

The Chairman now gave the floor to Mr. Overbeek.

Concerning the protective and sensitizing action of hydrophilic colloids on hydrophobic sols

by

J. Th. G. Overbeek (Utrecht).

1. *Protective action.*

It is a well known phenomenon, that the flocculation of a hydrophobic sol is hampered by the addition of a hydrophilic colloid, and a lot of experimental work has been carried out on the subject, the results of which in several cases have been applied to practical purposes. An example may be found in several pharmaceutical preparations, in which dispersion of a substance is maintained by the addition of a protective colloid (e.g. Collargol); whilst organic chemistry occasionally applies protective action, when carrying out reductions by means of colloidal Pd, where gum arabic effects the protection of the Pd.

Systematic investigations in this field were initiated by Zsigmondy[1]) who introduced the principle of "gold-number", which, though an arbitrary unit, enabled him to study the phenomenon in a quantitative way.

The gold-number represents the number of milligrams of substance, necessary for the protection of a fixed quantity of a certain gold sol (10 cm^3 containing 0.6 mg of Au) against the flocculating action of a considerable excess of NaCl solution. Gold-numbers may vary between 0.01 for gelatine and 25 for starch, all hydrophilic substances exerting a more or less pronounced protective action.

It has been established, that the behaviour of protecting agents towards various hydrophobic sols is similar to that towards the gold sol; consequently a small gold-number of a certain hydrophilic colloid in general also implies a strong protective action with any suspensoid.

Zsigmondy[2]) assumed that protective action might be due to a mutual union of lyophilic and lyophobic particles. Since lyophilic particles are usually much smaller than lyophobic ones, this assumption resolves itself in most cases in an envelopment of the latter by the former; consequently the surface of the lyophobic particles is composed of a layer of less easily flocculating material, like gelatin, gum arabic, or such like.

Zsigmondy's assumption is substantially supported by results of experimental work on the electrophoretic velocity of protected sols. Several investigators examined the electrophoretic velocity of sols and suspensions on addition of lyophilic colloid; by increasing the concentration of lyophilic colloid the observed electrophoretic velocity approaches a constant value, the electrophoretic velocity of the lyophilic substance. An example of this effect may be found in the work of Bendien[3]), who studied the influence of gelatin on gold sol at various p_H. His results are shown in fig. 1.

The same author also investigated the influence of other lyophilic colloids (e. g. dextrine, gum arabic) and found their behaviour to be closely similar to that of gelatin[4]).

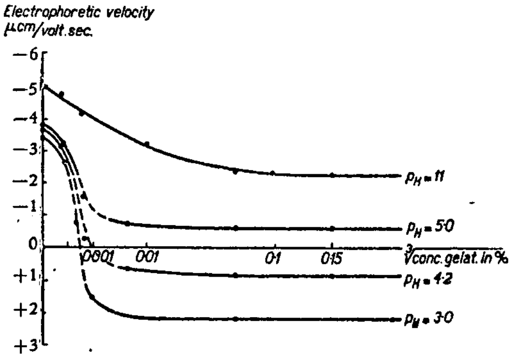

Fig. 1.

Attention must be drawn to the fact, that in all these cases the electrophoretic velocity of the lyophilic colloid is smaller than that of the suspensoid particles, which clearly indicates, that the increase in stability cannot be due to an increase in ζ-potential of the particles.

It has not been definitely established, which portion of the curve represents the range where protective action occurs. From the investigations of Bendien the impression prevails, that the range of protection coincides with the flat portion of the curve; an accurate investigation of the problem, carried out with a reliable technique, however, is still lacking.

If one compares the protective action of a certain quantity of hydrophilic colloid against the flocculating power of ions of various valency, then it is found, that protection is highest in the case of the strongly flocculating ions of high valency: i.e. protective action tends to minimize the Schulze—Hardy rule.

Table 1*).

Flocculation value of Carey Lea's silver sol in mixtures with gum arabic.

Gum arabic in mg/*l*.	Flocculation value in m mols/*l*.		
	NH_4NO_3	$Sr(NO_3)_2$	$La(NO_3)_3$
0	21	0.52	0.026
20	—	0.54	0.037
40	—	0.59	0.047
100	—	0.64	0.079
200	21	0.86	0.21
300	—	1.2	0.58
400	37	1.5	1.16
1000	>99	8.6	—

*) H. Freundlich and E. Loening, Kolloid-Beihefte **16**, 1 (1922).

A maximum value for the thickness of the protecting layer may be computed on the assumption of a total adsorption of the lyophilic substance by the suspensoids particles. In the case of gelatin and gold sol a value is found of 8 Å at the concentration of the gold number; for albumin and quartz particles, 4 Å at the beginning of the flat part in the electrophoresis

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[1]) R. Zsigmondy, Z. anal. Chem. **60**, 697 (1901); R. Zsigmondy-Thiessen, Das kolloide Gold, Leipzig, 1925, p. 173.

[2]) R. Zsigmondy, Verh. Ges. Naturf. Ärzte (Hamburg) 1901, 168.

[3]) W. M. Bendien, thesis Delft, 1926; W. Reinders and W. M. Bendien, Rec. trav. chim. **47**, 977 (1928).

[4]) Also c.f. H. Freundlich and H. A. Abramson, Z. physik. Chem. **133**, 51 (1928); H. Limburg, Rec. trav. chim. **45**, 875(1926).

curve (Abramson and Freundlich, l.c.). These numbers may point to the conclusion that proteins are spread on the solid substratum in a rather flat position.

We thus come to the conclusion that in protected sols the original double layer has lost most of its importance. The sol has adopted the peculiarities of the lyophilic colloid in all respects, while only the nucleus of the particles happens to consist of foreign material.

2. *Sensitizing action.*

It has been found that there is another phenomenon, which may occur in systems containing hydrophilic as well as hydrophobic colloids: i.e. sensitization.

On careful examination of the effect of addition of small quantities of lyophilic colloid to a suspensoid, it may be noticed that not only a protective influence is lacking, but a de-stabilizing action may even be involved. The flocculation value becomes smaller than that of the original sol and may even decrease to zero.

This sensitization has been observed in widely divergent systems and seems to be just as general a phenomenon as the protective action. Apparently sensitization often escaped the attention of the investigators who, being in search of the presence of a protective action, may have been inclined to be only interested in the behaviour of their systems on addition of an electrolyte concentration exceeding the flocculation value. In that case, sensitization, no influence and weak protection are liable to be summarized under the heading: "no protective action".

In order to obtain a complete picture of the interaction of lyophilic and lyophobic sols it is imperative to determine the flocculation value at all concentrations of lyophilic substance. Fig. 2 shows the changes of the flocculation value of AgI sol on addition of gum arabic[5]).

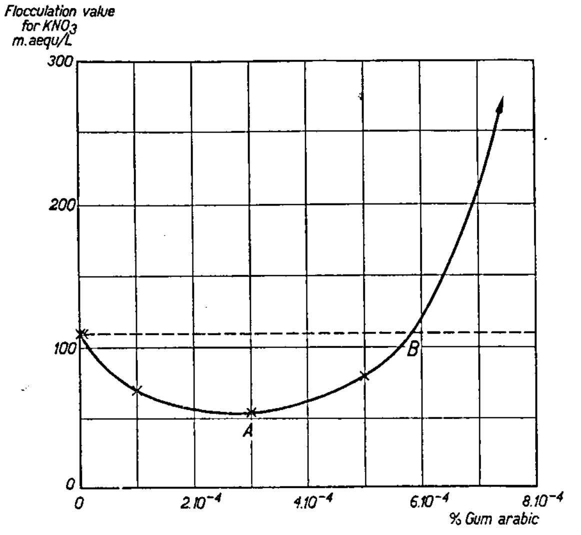

Fig. 2.

Until B sensitization occurs, which is maximum at A. At concentrations exceeding B protective action is present. The flocculation value in the minimum (A) of the curve may vary between the flocculation value of the original sol (i.e. no sensitization at all) and 0 (i.e. spontaneous flocculation).

The concentration of lyophilic colloid at which the minimum A occurs is usually a very low one. An AgI sol of 5 millimols/*l* is sensitized by 2 mg of gum arabic per *l*. The maximum sensitization of a 0.01 % gold sol is brought about by 0.0005 % of gelatin, the influence of 0.00005 % of gelatin still being detectable.

The electrophoretic velocity of sensitized sols appears to coincide with the downward portion of the curves of fig. 1. The dotted portion of these curves indicates the zone of sensitization. It may seem reasonable to attribute the decline of stability to a decrease of the ζ-potential assuming the influence of the increase in hydrophilic stability at such small concentrations of lyophilic colloid still to be negligible. Unfortunately the literature on the subject provides hardly any evidence for checking this assumption. Records of measurements of electrophoretic velocity and stability in the zone of sensitization are given bij Bendien and Limburg. From the work of Limburg (l.c.) the following data may be collected, concerning sensitization of oil emulsions by gelatin. In table 2 have been summarized those gelatin concentrations, which produce the same electrophoretic velocity of 3.5 at various p_H. At p_H 5.5 the corresponding gelatin concentration lies well within the boundaries of the sensitization zone. Consequently a disproportionately low stability is exhibited in that case, while the stabilities observed at p_H 2.8 and 4.7 show that an electrophoretic velocity of 3.5 by itself does not necessarily involve low stability.

Table 2.
Sensitization of oil emulsions by gelatin.

p_H	% gelatine	electrophoretic velocity	Stability
2.8	0	—3.48	0.40
4.7	0	—4.41	0.71
5.5	0	—4.67	0.74
2.8	0	—3.5	0.4
4.7	0.000001	— 3.5	0.5
5.5	0.00006	—3.5	0.2

This means that no support is gained for the assumption, that decrease of the stability should be due entirely to a decrease in ζ-potential. On the other hand neither do these numbers provide a definite disproval of the assumption.

What all this boils down to is an urgent need of more experimental work with well defined material (e.g. AgI sol and gum arabic) and a reliable technique. At present it seems advisable to consider whether another explanation may better fit the facts.

In those cases where sensitization is most obvious, i.e. where the flocculation value drops to zero, the charge of the lyophilic and lyophobic particles always appears to be of opposite sign. The negative gold sol is flocculated by a minute concentration of gelatin if the p_H is smaller than 4.7. Brossa and Freundlich[6]), made extensive investigations on

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[5]) Unpublished results obtained by C. Horsting.

[6]) A. Brossa and H. Freundlich, Z. physik. Chem. 89, 306 (1915).

mixtures of positive $Fe(OH)_3$ sol and negative serum albumin.

They observed that a certain quantity of serum-albumin is flocculated by a small quantity of $Fe(OH)_3$ but that the precipitate dissolves in excess $Fe(OH)_3$. With such a sol-mixture, containing an excess $Fe(OH)_3$, flocculation experiments were carried out.

The flocculation value is usually smaller than that of the original $Fe(OH)_3$ sol, which indicates that the sol has been sensitized but, on increasing the concentration of electrolyte, a second zone is reached where stability prevails; c.f. fig. 3, in which the abscissa represents concentrations of electrolyte and the ordinate the degree of flocculation in arbitrary units.

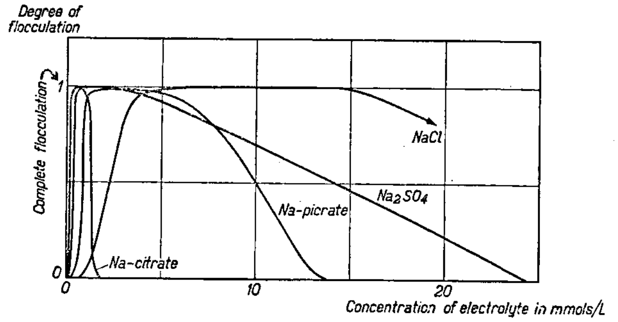

Fig. 3.

The sequence in which electrolytes of various valency flocculate and restabilize the $Fe(OH)_3$ sol shows a striking resemblance to the way in which electrolytes affect the stability of complex coacervates. If namely a coacervate is made containing an excess of particles of one charge then the first addition of electrolyte will cause an increase of turbidity while a further increase of the amount of electrolyte will bring about the disunion of the coacervate due to lack of oppositely charged particles.

Figure 4 represents the influence of a neutral salt on the degree of turbidity of mixtures of lecithin and gelatin at a p_H of 2.89. The initial coacervate (salt concentration 0) is positive, i. e. contains excess of gelatin [7]).

This assumption brings all the results of Brossa and Freundlich into agreement. The precipitate contains $Fe(OH)_3$ as well as albumin; pure albumin is negatively charged; the mixture with $Fe(OH)_3$ is positive, owing to the excess of $Fe(OH)_3$; the stable sol at high concentration of electrolyte is negative.

It may seem surprising that $Fe(OH)_3$ behaves like a hydrophilic sol but this may be explained by the assumption, that in the zone of stability at high salt-concentration the $Fe(OH)_3$ particles are protected by albumin.

There are a great number of cases, where sensitization can be explained as mutual flocculation. Oil emulsions are flocculated by small quantities of gelatine, if the p_H is smaller than 4.7 (Limburg l.c.) $Fe(OH)_3$ sol is sensitized by amylum, glycogen, saponine. In several of the cases where sensitization of negative sols (SiO_2, mastix, Ag, Au; As_2S_3, V_2O_5, etc.) was brought about by proteins, there is considerable probability, that the p_H was on the acid side of the isoelectric point; consequently in those cases also mutual flocculation may have been involved [8]).

For the characterization of this phenomenon Zsigmondy introduced the principle of: "Umschlagzahl" [9]) (U-number).

The U-number represents the number of milligrams of sensitizing substance necessary in order to effect a change of colour from red to violet with a certain amount of an *acid* gold sol. For proteins these U-number are about 0,002—0,004 (the gold number of gelatin is 0,005—0,01).

Although mutual flocculation frequently underlays the phenomena described in the literature, this mechanism cannot be held responsible for all the cases of sensitization which are known at present; because there are a number of cases, in which an unsuspected negative suspensoid is sensitized by a lyophilic colloid of equally well known negative charge.

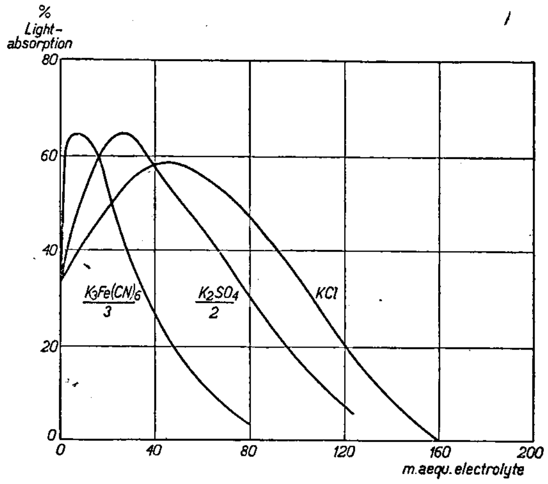

Fig. 4.

In the reaction of Lange (1912) between gold sol and cerebro-spinal liquid the phenomena involved are dominated mainly by the sensitization of gold sol by albumin and globulin of the same sign [10]).

In the work of Bendien and Limburg examples may be found of sensitization of gold sol and oil emulsions respectively by gelatin at a p_H higher than 4.7 in this case by negative gelatin.

Much more convincing, however, than these cases of sensitization by an amphoteric colloid, in which one may still be inclined to leave open the possibility of opposite charges being involved (e.g. locally situated) is the sensitization of negative colloids by gum arabic or amylose.

A very interesting example of a technical procedure applying this mechanism may be found in the process of Henry [11]) in which the liquid, used for washing coal, which contains a very tenacious coal suspension is rapidly flocculated on addition of starch and lime (i.e. $Ca^{\cdot\cdot}$ ions). De Smet [12]) made

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[7]) H. G. Bungenberg de Jong and R. F. Westerkamp, Biochem. Z. **234**, 386 (1931).

[8]) For a summary c.f. S. Ghosh and N. R. Dhar, Kolloid-Z. **41**, 229 (1927).

[9]) Zsigmondy and Thiessen, Das kolloide Gold, Leipzig, 1925, 191 etc.

[10]) c.f. Joel, Das kolloide Gold in Biologie und Medizin, Leipzig, 1925, p. 32, 59.

[11]) R. A. Henry, Chem. Zentr., 1936, I, 1476, French patent 787831.

[12]) M. de Smet, Natuurw Tijdschr. **18**, 118 (1936).

further investigations of this process. He was able to show that finely ground anthracite has a negative charge. In addition he found that amylum Merck (free from proteins) was as well suited for sensitization as potato starch.

Negative AgI sol may also be sensitized by amylum and gum arabic, as has been shown in fig. 2.

Thus in classifying the interaction between lyophilic and lyophobic colloids a distinction must be made between three cases — which distinction was also maintained by Zsigmondy for gold sol — namely:

1. above a certain concentration protective action occurs irrespective of the sign of the charge;

2a. Below that concentration mutual flocculation occurs with opposite sign of charge; b. if sign of charge is similar sensitization frequently occurs at such small concentrations.

H. Freundlich[13]) suggested that sensitization might be due to a reaction between lyophilic colloid and the peptizing electrolyte of the suspensoid. For the sensitization of $Fe(OH)_3$ sol by proteins this explanation is consistent with the well known fact, that proteins are able to bind $Fe^{\cdots}$ ions and that according to Lindau[14]) its capacity of binding iron runs parallel with its capacity of sensitizing $Fe(OH)_3$ sols.

It does not follow however that this mechanism should be accepted in explanation of sensitization in general. It does not hold for instance in the cases AgI-starch, AgI-gum arabic, and coal-starch, where a reaction with the peptizing electrolyte is not only rather improbable, but even contradictory to the experimental facts. In the experiments of De Smet concerning coal and starch the p_H is not altered on addition of the starch. According to electrometric determination neither starch nor gum arabic affect the *concentration of I′ ions* of dilute KI solution or AgI sol. Thus only the explanation first suggested by Zsigmondy remains. The two colloids exhibit an appreciable tendency to unite irrespective of their charge. This is obvious from the protective action where envelopment of the lyophobic particles occurs. Now the same tendency will be in operation between lyophilic and lyophobic particles at small concentrations of the former; in this case, however, the suspensoid particles will tend to envelop the lyophilic ones, which leads to a decrease of the stability of the suspensoid particles. A very schematic picture is shown in fig. 5, where a square represents a gold particle and a circle a gelatin particle.

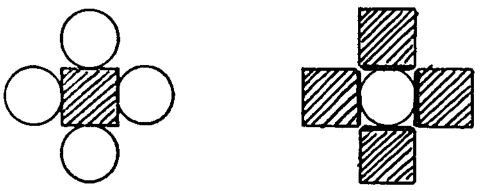
Protection. Sensitization.

Fig. 5.

Even though this explanation seems rather attractive and generally applicable, and provides us with an elegant explanation of the influence of the size of the particles[15]) of lyophobic and lyophilic colloid, there ar two facts which require a more detailed explanation.

In the first place under the ultramicroscope no difference is observed between the original AgI sol and the same sol after such a quantity of amylum or gum arabic has been added that maximum sensitization is brought about. Neither Brownian movement nor the number of particles have been affected in any respect. Consequently it is not allowable to conclude that aggregations have been formed consisting of more than one AgI particle.

In the second place it must be born in mind, that sensitization (as well as protection) is not independent of the nature of the flocculating ion. Sensitization and protection occur in smaller concentration of lyophilic colloid if flocculation is brought about by ions of high valency; e.g. point B (fig. 2) in the case of addition of $Ce(NO_3)_3$ to AgI sol is reached at a concentration of gum arabic ten times smaller than if KNO_3 is used as a flocculating agent.

In addition, sensitization is far less intensive in the case of $Ba(NO_3)_2$ and $Ce(NO_3)_3$ than of KNO_3. (The depth of the minimum A is less in these cases).

A similar behaviour was observed in the case of alkali-blue and tannine by Freundlich and Mitsukuri[16]) and in the case of SnO_2 and As_2S_3 with tannine and gelatin as sensitizers by Ghosh and Dhar[17]).

We are thus inclined to assume, that until electrolyte is added aggregates consisting of *one* suspensoid particle with one or more lyophilic particles are formed; the double layer, however, maintains its capacity of exerting such repulsive action that these complexes cannot aggregate further; the image in the ultramicroscope will therefore remain unchanged.

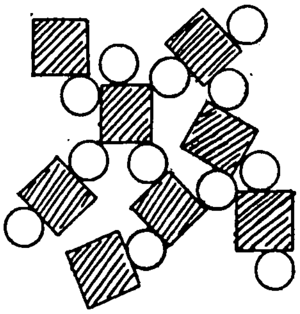
Flocculation of a sensitized sol.

Fig. 6.

Apparently the formation of these complexes is promoted by the presence of polyvalent ions; which is not too surprising, since by addition of such ions positive charges may come into operation on the surface of the particle which will attract gum arabic; consequently sensitization may occur at smaller concentration of electrolyte.

If the concentration of electrolyte is increased till flocculation of the sensitized sol occurs, aggregates

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[13]) H. Freundlich, Kapillarchemie II, 471, Leipzig, 1932.

[14]) Lindau, Biochem. Z. **219**, 385 (1930).

[15]) R. Zsigmondy and E. Joel, Z. physik. Chem. **113**, 299 (1924).

[16]) Freundlich and Mitsukuri, Kolloid-Z. **39**, 123 (1926).

[17]) S. Ghosh and N. R. Dhar, Kolloid-Z. **41**, 229 (1927).

will be formed in which AgI particles alternate with gum arabic particles, as is schematicly represented by fig. 6.

This may serve as an example of a case in which flocculation is induced not only by a decrease of the mutual repulsion, but also by an increase of the attraction (caused by the tendency of the lyophilic colloid to occupy the interface AgI-water)[18].

No explanation has been given of the fact, that sensitization is less intense when flocculation is brought about by polyvalent ions.

Attention must be drawn to the importance of sensitization in practice. The example of coal-starch in which sensitization induced a rapid flocculation of a tenacious lyophobic suspension has been mentioned before.

The opposite procedure has been applied as well; Michaelis and Rona[19]) developed a method for freeing solutions from proteins by precipitating the protein by the addition of a mastix suspension.

In methods for the purification of sewage sensitization may frequently play a part.

It has frequently been observed, that flocculation of sensitized sols leads to the formation of flakes, which settle very quickly, and this property makes these systems particularly attractive for practical application.

Until now the systems under consideration always contained one lyophobic and one lyophilic component. If both of the sols are of the lyophobic type, real protection and sensitization are not to be expected, since the particles exert no particular attraction on one another.

We may find traces of sensitization in the case of sols of opposite charge ($Fe(OH)_3$ and As_2S_3), sensitization caused by chemical reaction (As_2S_3 and the S-sol of Odén) or minor protection by chemical reaction (AgI sol and gold-sol)[20].

3. *Summary.* In the preceeding lines we have aimed at giving a review of the phenomena involved in the interaction of lyophilic and lyophobic colloids and we have tried to give an explanation of these facts. This is a rather detached domain of the dynamics of hydrophobic colloids in which the influence of the double layer is considerably reduced.

Substantially the phenomena are dominated by a strong attraction between lyophilic and lyophobic particles, irrespective of the sign of their charge. They combine with each other in all concentrations while it depends on the proportion of the concentrations whether this will result in protection or in sensitization.

If the two colloids are of opposite charge, or if they are liable to react with each other, the results will be superimposed on the phenomena in general.

Discussion.

Dr. Pieters remarks: In Henry's process so much lime is added that the effect of the addition of starch becomes practically negligible. Nevertheless the effect of very small amounts of starch on the flocculation of fine suspensions is often very striking. In this respect I should like to draw the attention of Mr. Overbeek to the observation we made that by the addition of starch to the effluent of a coal washery, the coarser particles are readily precipitated, while the finer and colloidally dispersed matter is apparently unaffected. It would be of great interest to devise a means of explaining this behaviour of the starch sol.

Prof. Kruyt says: Ir. de Groot of Oranje-Nassau-mine claims, that not a single component of the Henry-mixture can be missed to get a satisfactory clearing of sewage water. De Smet (Gent) started his research with a suspension of anthracite to which he added starch; then we took gum arabic and later on sodium arabinate in stead of starch and at last AgI in stead of coal, thus continuously simplifying the model. In every case we found the sensibilisation with very small amounts of the hydrophilic colloid. Horsting completed the investigation as mentioned in Overbeek's paper.

Mr. Overbeek means: It might be of interest to compare the behaviour of fine and coarse coal particles with that of fine and coarse Au-sols, as described by Zsigmondy and Joel[*]. The coarser Au-sols appear to be sensitized by smaller concentrations of gelatin than the finer ones.

Dr. Limburg is of the opinion, that the sensitization of f.i. an oil emulsion when adding increasing amounts of gelatin can still be explained by the two factors, which work in opposite directions, viz. the decreasing charge of the particles and the increasing stabilisation by the gelatin-film. It is not clear why the data collected in table 2 of Mr. Overbeek's paper should plead against this theory. They only show, that with *different* concentrations of gelatin, the charge of the particles is not the only factor which governs the stability. This however is the very starting point of the above mentioned theory.

Also sensitization of a negatively charged sol by a negatively charged lyophilic colloid is not in contradiction with this theory. In all those cases in which determinations of the cataphoretic velocity have been carried out, the lyophilic colloid decreased the charge of the sol particles (cf. Limburg, Rec. trav. chim. **45**, 875 (1926); Reinders and Bendien, Rec. trav. chim. **47**, 976 (1928)). At small concentrations of lyophilic colloid the charge decreasing effect is stronger than the stabilising effect. Hence the stability is decreased and sensitization results.

Mr. Overbeek answers: In Dr. Limburg's train of thought, two emulsions carrying an *equal* charge, at *different* concentrations of gelatin would have a different stability, the emulsion containing the greater amount of gelatin being the more stable. Table 2 shows the opposite to be the case. At p_H 5.5 the stability is low at a relatively high concentration of gelatin.

This indicates, that there must be another factor, besides the lowering of ζ, which diminishes the stability of sensitized sols.

Mr. Sarluy asks: In experiments with electrodialysed hydrophobe sols and protein sols Pauli

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[18] c.f. H. C. Hamaker, Rec. trav. chim. **56**, 745 (1937).

[19] Michaelis and Rona, Biochem. Z. **2**, 219 (1907); **3**, 109 (1907); **4**, 11 (1907); **5**, 365 (1907); **7**, 329 (1908); **8**, 350 (1908); **13**, 121 (1908); **14**, 476 (1908).

[20] H. R. Kruyt and C. A. Nierstrasz, Kolloid-Z. **78**, 26 (1937).

[*] R. Zsigmondy and E. Joel, Z. Physik. Chem. **113**, 229 (1924).

found, that in the absence of electrolytes protective action never occurs. What, according to the speaker, is the role of minute quantities of electrolytes in the mechanism proposed by Zsigmondy, and what is the speaker's opinion about Pauli's experiments?

Mr. Overbeek says: In all probability the absence of protective action in Pauli's experiments must be explained by the acid reaction of electrodialysed sols. This gives rise to a positive charge of the protein, so that mutual flocculation may result.

Dr. Müller says:

1. Was calcium hydroxide added in De Smet's tests, and, if so, was the carbon suspension still negative after this addition?

2. You said that in sensitization, aggregates of one suspensoid particle with one or more lyophilic particles are formed, the repulsive force between the suspensoid particles remaining the same, however. But does not this repulsive force become smaller because the lyophilic particles partly shield the charge of the suspensoid particles?

Mr. Overbeek answers:

ad 1. De Smet investigated the behaviour of carbon suspensions with $Ca(OH)_2$ and $CaCl_2$. He did not found any indication that the $Ca^{\cdot\cdot}$ ion may effect a reversal of the charge of the suspension.

ad 2. I only maintained, that before the addition of electrolyte to a sensitized system, the repulsive force must be strong enough to keep the hydrophobic particles apart. This repulsive force may be smaller than it was in the original sol.

Dr. de Boer remarks: Is the following hypothesis permissible in explanation of sensitization? If the hydrophile substance is strongly bound by its hydrophile groups (for example the CO—NH-groups in gelatin) to the surface of the hydrophobe particles, and thereby pushes aside ions of the double layer, a condition might be reached where, (with very small amounts of hydrophile substance which may be entirely bound in the above manner), the hydrophile character is not yet able to manifest itself, while at the same points a double layer capable of repulsion is no longer present, and the particles may attach themselves. Upon addition of more hydrophile substance, it will also be added at these points but now with the hydrophile groups outermost, so that a shielding action is obtained. The charge of the hydrophile substance is then indeed of no importance, but only the hydrophile groups.

Mr. Overbeek answers: It seems rather improbable, that, at the interface water-X (a hydrophobic substance) a hydrophil particle should turn its hydrophilic groups to X rather than to the water.

Apart from this, the picture, Dr. de Boer suggests of a sensitized flocculation does not differ very much from the one given by me. In both cases the hydrophobic particles are held together by hydrophilic ones.

In my theory this linkage is effected by *one* hydrophilic particle, in Dr. de Boer's theory by *two*.

It seems to be premature to enter into such details as long as experimental data in this field are still scarce (exp. data concerning the amount of hydrophilic substance carried down by the flocculating sol are almost completely lacking).

Mr. Nanninga asks: With this explanation of sensitization can you account for the phenomenon first observed by Rideal in a hydrogenation process [21]) and verified by me in the decomposition of H_2O_2, that the catalytic activity of a platinum sol increases, when very small quantities of gelatin (e. g. 0.00075 % with a 0.02 % sol) are added?

Prof. Kruyt says: As the heterogeneous catalysis is located at the "Lockerstellen" (Taylor), Rideal's results, as mentioned by Mr. Nanninga would suggest, that the lyophilic colloid is not bound at those spots but just the contrary at the flat faces.

Dr. Boasson wants to draw attention to a group of sensitization-phenomena, which are as remarkable as those discussed here in as far as they occur between two hydrophilic colloids (especially proteins) with charges of the *same* sign. I mean the sensitization-phenomena well known in serology and immunology. For this case Marrack [22]) has already given the picture used by Overbeek for the flocculation of a sensitized sol (fig. 6). Moreover it has been found that here, too, the phenomena are largely governed by the laws of complex coacervation [23]).

Disregarding the marked specificity of serological reactions, an analogy with the system silver iodide-gum arabic seems to be well established. Would it be possible to use the latter system as a model for serological flocculations?

Mr. Overbeek answers: If serological flocculations are hampered by large concentrations of electrolyte there seems to be no advantage in using the sensitization of AgI by gum arabic as a model, as in this system no stability zone is found at higher saltconcentrations.

After the conclusion of this paper Dr. van der Minne was called upon by the chairman to present two subsequent papers, a more general and a more specialized one.

General remarks on emulsions *)

by

J. L. van der Minne (Amsterdam).

In the last two decades emulsions have been studied very intensively and a mass of literature has grown up on the subject. This being so, however conscientiously I might attempt to summarize it, my resumé could be no more than an extract of the findings elaborated by many different authors. I therefore propose instead to concentrate here on a few important points relating to the emulsification and stability of emulsions, with special reference to the physico-chemical principles.

We give the term "emulsion" to a system of two

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[21]) Rideal, J. Am. Chem. Soc. 42, 749 (1920).

[22]) J. L. Marrack, The Chemistry of Antigens and Antibodies, London, 1934 (page 106).

[23]) E. H. Boasson, Dissertation, Utrecht, 1937, and J. Immunology, in press.

*) For collective literature on emulsions see:
W. Clayton, The theory of emulsions and their technical treatment, London, 1935, 3rd ed.; O. Lange, Technik der Emulsionen, Berlin, 1929; Brit. Section Intern. Soc. Leather Trades' Chem., Technical aspects of emulsions, London, 1935; in Dutch: Van der Minne, „Over emulsies", Thesis, Utrecht, 1928.

unmiscible liquids, one of which is distributed in the other in a more or less finely divided state. The two phases are often designated as oil and water, although water needs not necessarily be one of the phases; nevertheless, in the majority of cases studied it is. The division of the phases may be such that the oil is dispersed in the water, but it may also be the other way about, i.e., "water in oil", and mixtures of the two systems also sometimes occur. Two pure liquids only produce an emulsion in which one of the phases is present in a very small quantity. For a closer description we shall take these very dilute emulsions and the concentrated emulsions individually.

A. *Very dilute emulsions.*

If pure liquids are used, these emulsions usually do not contain more than 0.01 %, at most 0.1 % of disperse phase. They are formed when the two liquids are shaken together; also sometimes when they are distilled together, in which case they are formed in the condenser. These systems have often been the subject of colloid-chemical investigations; they were regarded as the prototype of a colloid. Ellis[1]) and Powis[2]) devoted those celebrated investigations to them which opened up the knowledge of the influence of the electro-kinetic potential upon the stability of colloids. Limburg[3]) and the present author also included these systems in their research. It has transpired that the stability (in the sense of durability) of these emulsions depends upon:

a. The electro-kinetic potential;
b. The interfacial tension;
c. Some properties of the intermicellar phase which are connected with the presence of electrolytes. (Limburg[3]) states that electric conductivity is important and Eilers[4]) stresses the thickness of the electric double layer);
d. The solubility of the two components of the emulsion in each other also appears to be a matter of importance.

The particle sizes of these emulsions are from 1 to 10 microns. The life of emulsions in a more finely divided state is so short that it is scarcely possible to study them. But also the emulsions of 1 to 10 microns can only exist at room temperature for a few days, even if creaming or sedimentation is prevented.

It is a remarkable fact that these systems and the more concentrated emulsions to be discussed below are coarser than the systems with which colloid chemistry is generally concerned.

To make more durable emulsions with a larger percentage of disperse phase, a third substance is required, called the „emulsifier". Thus we come to the discussion of

B. *The more concentrated emulsions.*

By this we mean the emulsions containing from 0.1 % to 90 % and more of disperse phase. Such emulsions can be made by vigorously agitating the two liquids, but the presence of an emulsifier is necessary to maintain these systems after agitation has ceased. The nature of this emulsifier also decides which of the two liquid phases is to be the disperse phase. In 1913 Bancroft[5]) formulated a law, the gist of which is that the phase which this emulsifier keeps in solution or, which it moistens best, will become the outer phase of the emulsion. The kinds of substances that do duty as an emulsifier are very various, but they all have to be adsorbed to the interface in some degree. With the exception of fatty acids, which are moleculary soluble in the oil phase, moleculary soluble substances are, so far as is known, not emulsifiers.

Examples of various emulsifiers for the two types of emulsion are given below. By "oil" we mean the liquid phase that does not mix with water. The emulsifiers are given in three classes in the order of diminishing degree of dispersion.

Emulsifiers.

For oil-in-water emulsions.	*For water-in-oil emulsions.*
I. *Colloidal electrolytes.*	
Alkali soaps. Salts of ammonia and of alkali metals of the higher fatty acids, naphthenic acids and sulphonic acids.	Magnesium, alkaline earth metal and heavy metal soaps of the higher fatty acids, naphthenic acids and sulphonic acids (in so far as insoluble in water).
II. *Lyophilic colloids.*	
Albumins: gelatine, casein Carbohydrates: agar	The same after they have been dehydrated by the addition of phenols or tannins, and have acquired a more oleophilic character
Saponin	Dammar resin.
III. *Finely divided solids.*	
E.g. basic sulphates of copper, nickel and iron	Carbon.
Calcium carbonate	Mercury sulphide and lead sulphide.
Clay	Clay.

Note to III.

Emulsions prepared with such emulsifiers were first made by Pickering[6]). As with the other emulsifiers mentioned, it is essential that these finely divided solids shall accumulate in the interface. If two liquids are shaken with different powdered solids it will be observed that the latter are divided in different ways between the two phases, all according to the nature of the solids. Reinders[7]) and Hofmann[8]) have investigated this matter. They found that these substances are often adsorbed by the interface and that besides this they often show a preference for one of the phases in which to disperse. If finely enough divided, the substances which collect in the interface may do the work of an emulsifier.

A few substances, one of which is clay, may stabilize both oil-in-water and water-in-oil emulsions; it depends upon the history of the material, viz., whether it has been wetted first by one or the other liquid, and also upon chemical factors, which may also affect the "wetability".

While further particulars regarding the emulsifiers we have just given can be found in the literature, we should like to make a few special comments here.

The properties of the emulsions are governed by the properties of the emulsifier. For example, the

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[1]) Ellis, Z. physik. Chem. **78**, 321 (1911) and **80**, 597 (1912).

[2]) Powis, Z. physik. Chem. **89**, 91, 179, 186 (1915).

[3]) Limburg, Rec. trav. chim. **45**, 772, 854 and 875 (1926).

[4]) Eilers, Chem. Weekblad **33**, 358 (1936).

[5]) Bancroft, J. physik. Chem. **17**, 515 (1913).

[6]) Pickering, J. Chem. Soc. **91**, 2001 (1907).

[7]) Reinders, Kolloid-Z. **13**, 235, 19 (1913).

[8]) Hofmann, Z. physik. Chem. **83**, 385 (1913).

oil-in-water emulsions of Class I are not stable in the presence of calcium salts and acids if the soaps themselves are not resistant to them, as in the case of the normal higher fatty acids and naphthenic acids. As a rule the emulsions of Class II are resistant to various electrolytes, because, as lyophilic colloids, the emulsifiers are resistant to them. With Class III, where the finely divided solids form, as it were, a mechanical shell (see below), one usually finds great stability towards electrolytes. There are exceptions however. An emulsion for which freshly precipitated calcium carbonate was the emulsifier was found to be very sensitive to electrolytes; the influence of the valency of the cation was clearly apparent and this pointed to the fact that a certain negative electrokinetic potential is essential to the existence of the emulsion [9].

As to emulsification, we have just said that the fine dispersion should be obtained mechanically. This applies to all cases where the emulsifier is already in the outer phase of the emulsion before or during its manufacture. If a solution of, say, potassium oleate in water is combined with a liquid hydrocarbon — xylene, for example, — the two liquids maintain their individual existence. To make an emulsion of them it is necessary to stir them or shake them so as to obtain liquids finely divided in each other. Both forms of emulsion (oil-in-water and water-in-oil) are then formed but, since only one of the forms is stabilized by the emulsifier — in this case the oil-in-water emulsion — only this eventually persists.

The curious fact has been observed that, if the soap is formed during the process of emulsification owing to the addition of caustic potash solution (KOH) to the water phase and fatty acid to the oil phase, a far finer emulsion can be obtained with considerably less mechanical effort. The reaction between the fatty acid and the caustic solution, which takes place in the interface, seems greatly to assist emulsification. Under certain conditions spontaneous emulsification can be brought about in this way; the liquids emulsify without the assistance of mechanical movement, though some movement is necessary in order to bring newly formed interfaces into contact. In his article for this Symposium Eilers gives examples of this (under chemical emulsification). There is an alternative way of adding the emulsifier to the emulsion, that being to introduce the alkali soap, which dissolves best in the water phase, into the oil in a colloidally divided state (by some expedient, e.g., by the addition of alcohol or by using special soaps) When brought into contact with water, an oil thus previously treated also will spontaneously produce an emulsion of oil in water.

As regards stabilization by emulsifiers, in his thesis (1928) the author showed in a diagram how he imagined the emulsions were stabilized by emulsifiers (see fig. 1), with special reference to the stabilization of an emulsion by finely divided solids. He exemplified the case in which the solid particles are oleophilic, that is to say are wetted better by oil than by water. If one here makes a water-in-oil emulsion, there will be, as it were, a shell to prevent the vulnerable oil-water interfaces from coming into contact (left, fig. 1), while in the case of an oil-in-water emulsion these interfaces may touch and coagulation may take place [10]. In principle this conception also applies to the other classes of emulsifiers.

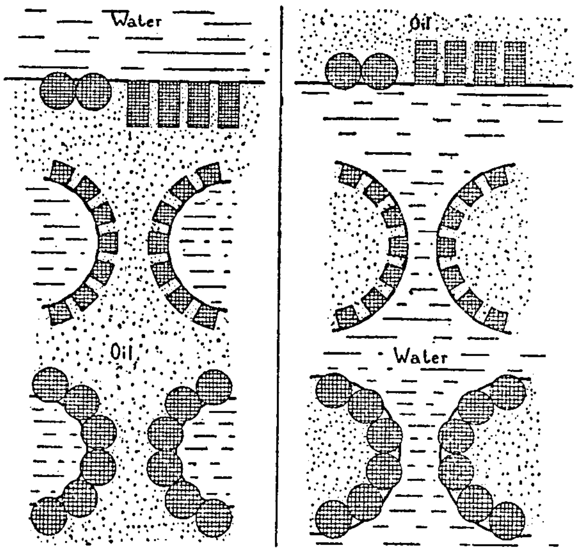

Fig. 1.

Regarding the class of finely divided solids it may be said that, up to a point, the more finely they are divided, the more effectual are they as emulsifiers. Beyond that critical point, however, the emulsifying action will again diminish [11]) and with colloids like arsenic trisulphide sol or the iron hydroxide sol, flocculating electrolytes have to be added to obtain emulsification [12]). It may be asked what the effect of these electrolytes is. Do they, by lowering the electro-kinetic potential of the oil and the colloid particle, break down any mutual repulsion between these two, or is it only the flocculating effect upon the colloid that is essential to emulsification? In a contributory paper investigations are recorded from which it may be inferred that the beneficial effect of electrolytes upon the emulsifying action of colloids is to be attributed to this flocculating action. It is still an open question whether this is to be explained by the assumption that the flocculated particles provide better adhesion in the interface, or whether the cohesion in the interface is stronger owing to the flocculation of the particles, the film thereby becoming more rigid, which is conducive to better emulsification (i.e., greater stability).

It should be added that the two different types of emulsifier as a rule counteract each other. If emulsifiers for one type of emulsion are added to an emulsion of the reverse system, the emulsion will tend to coagulate. But it also sometimes happens that two emulsifiers for the same type will nevertheless thwart each other, a phenomenon which is also observed in frothing. To give an example:

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[9]) See Thesis van der Minne, page 83.

[10]) At about the same time Ramsden gave similar figures in the second edition of Clayton's book and elaborated a theory which comes approximately to the same thing.

[11]) E.g. Bechhold, Kolloid-Z. **28**, 6 (1921).

[12]) Briggs, J. Ind. Eng. Chem. **13**, 1008 (1921).

The stability of a bituminous emulsion of the oil-in-water type containing clay as emulsifier can be substantially reduced by the addition of alkali soap which, in the case of a coarse emulsion, may lead to coagulation. These are important matters in the demulsification of water-in-oil emulsions, such as crude oil emulsions 13).

In conclusion let us examine the influence of a few factors individually.

1. *Electro-kinetic potential.*

With the dilute emulsions (see above), the electro-kinetic potential is of primary importance, but with the more concentrated emulsions it is of minor influence. Unaided, the electro-kinetic potential has not the power to keep such an emulsion intact, however high one makes it. The interfacial composition is far more important. With many lyophilic colloids it may be assumed that hydration is a factory of stability, but there are cases — e.g. with clay as the emulsifier — in which hydration, if any, is relatively slight, in spite of which the emulsions are resistant to electrolytes in large concentrations. The influence of the electro-kinetic potential is nevertheless detectable in some emulsions made with solids; for instance, in the emulsions discussed above with calcium carbonate as emulsifier.

2. *Interfacial tension.* Oil phase — water phase.

This factor, which affects the stability of dilute emulsions, in the sense that the lower the interfacial tension the greater is the stability of the emulsion, also takes a secondary place in the *stability* of the more concentrated emulsions. It tells in the preparation of the emulsion (in emulsification), in that it aids the breaking up of the liquids, but two pure liquids of low interfacial tension do not produce a concentrated, durable emulsion. Take, for example, ether and water or phenol and water in certain ranges of temperature not far from their critical solution temperature, where the interfacial tension may be lower than of two properly emulsifying liquids 14), in spite of which the former liquids do not produce a stable emulsion.

Good emulsifiability (in the sense of the formation and persistence of emulsion) and interfacial tension are nevertheless repeatedly connected in technical literature. This, however, is not because of the low value of the interfacial tension itself, but rather because a low interfacial tension points to the presence of substances which may act as an emulsifier. For, nearly all the emulsifiers of classes I and II are capillary-active substances and reduce the interfacial tension.

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13) See van der Minne, Proc. World Petroleum Congr., I, 516 (1933).

14) We here ignore the phenomena which occur in the neighbourhood of the critical solution temperature, where the interfacial tension approaches zero and the critical turbidity (which is attributed to a kind of emulsification) appears, because this is not really a case of two clearly demarcated phases.

Emulsification with lyophobic colloids

by

J. L. van der Minne (Amsterdam).

It is known that finely divided solids are utilizable emulsifiers (Pickering 1)). It is also known that the degree of dispersion of these solid, powdered substances is an important factor (see Bechhold). Colloidal solutions of lyophobic colloids have little emulsifying power. Briggs has observed that after the addition of slightly flocculant electrolytes emulsions can also be obtained with lyophobic colloids. To explain this one might assume either that the particle size, itself, of the colloid is responsible, as in the Bechhold case cited above, or that these coagulating electrolytes enhance the attraction or the repulsion between the oil-water interface and the colloid particles, thus making it easier for the latter to enter the interface. In a given case, viz., the emulsification of liquid paraffin (medicinal oil) in water by means of colloidal iron hydroxide, we studied the electrokinetic potential of the drops of oil and of the iron hydroxide as depending upon the addition of electrolytes, in order to find out which of the two possible explanations was the more probable.

Emulsions containing the same percentage of oil and water phase were made of a pure, freshly refined medicinal oil of 130 Centistokes viscosity at 20° C with an Fe_2O_3 sol of 0.5 % by shaking by hand in glass tubes. The electrolyte was added to the sol before this was mixed with the oil. The results are shown in figure 1. It will be seen that the following quantities of the various electrolytes are needed. We also give the flocculation values (after 2 hours) of the sol.

	Incipient emulsification	Flocculation value of the sol
NH_3	2—3 m.mol.	3.0 m.mol.
K_2SO_4	0.5—1.0 ,,	1.3 ,,
$K_3Fe(CN)_6$ . . .	0.5—0.75 ,,	0.85 ,,

It also emerged that the addition of large amounts of $Fe(NO_3)_3$ up to 100 m/mol. failed to bring about emulsification; nor did flocculation occur. The iron hydroxide sol was prepared from ferric nitrate by the addition of 0.9 of the equivalent amount of ammonia and dialysation until no more NO_3' could be identified. In this way a 10 % sol was obtained which was diluted with distilled water.

Applying Burton's method as amended by Janssen and Bendien 2), we determined the electro-kinetic potential both of the iron hydroxide sol and of a fine emulsion of medicinal oil in the intermicellar phase (separated from the iron hydroxide sol after the cited quantities of the various electrolytes had been added). The potential drop in the tube varied between 10 and 30 volts over the length of the U-tube (27 cm).

Where the oil is concerned a very dilute, but visibly turbid suspension (emulsion) had to be made

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1) See for literature references preceding paper.

2) Janssen and Bendien, Rec. trav. chim. 46, 11 (1927).

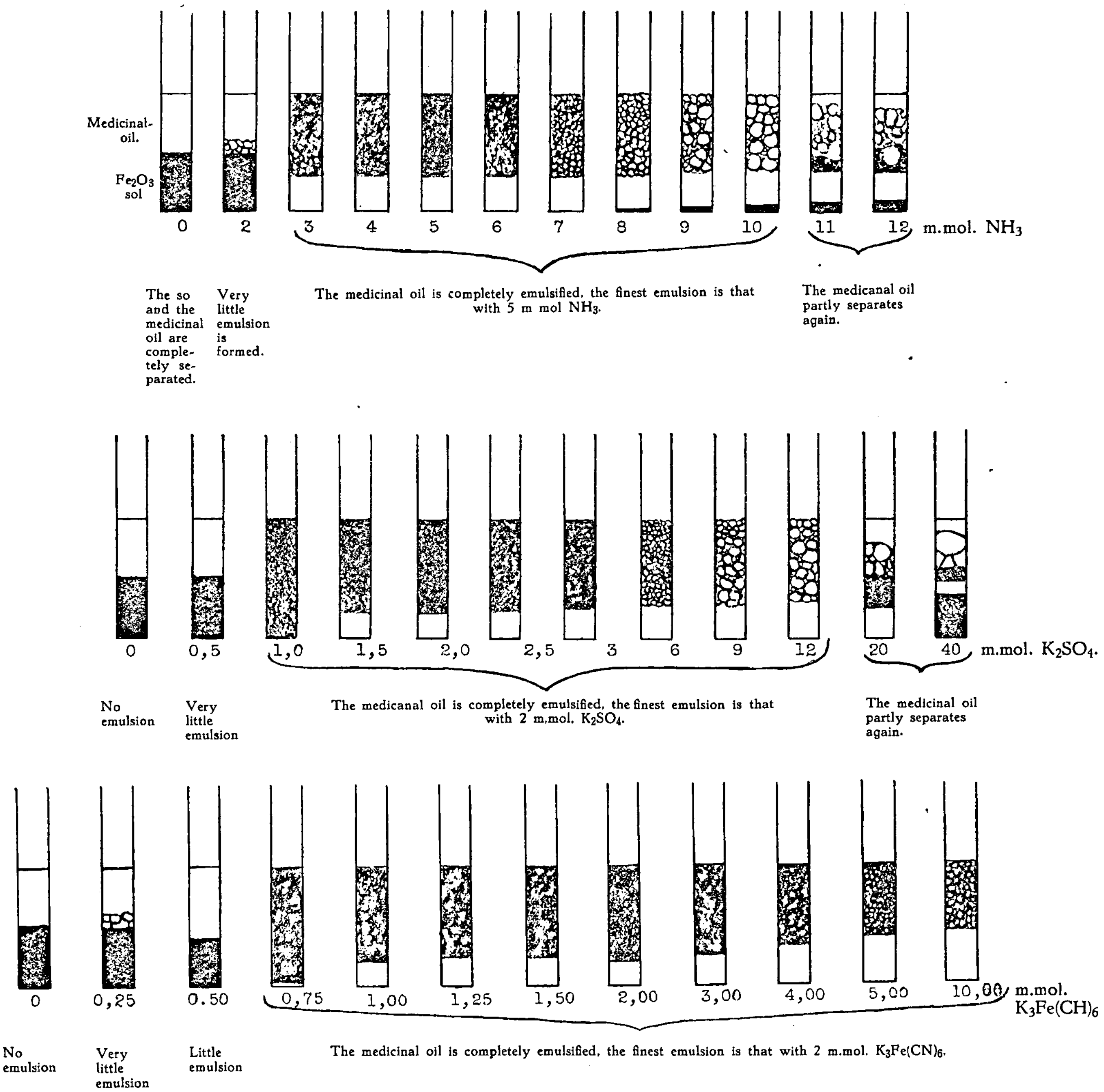

Fig. 1. Sketch of the emulsification of medicinal oil with Fe_2O_3 sol of 0.5 % to which different electrolytes are added the quantities of sol and medicinal oil are the same.

with these ultrafiltrates. This was done by shaking the ultrafiltrate together with the medicinal oil in a mechanical shaker for 24 hours. It was found that the medicinal oil used did not emulsify enough, apparently on account of its great purity. In order to overcome this difficulty we added a product insoluble in water (so that the aqueous liquid did not change), which facilitated emulsification. We added 0.02 % of dammar dissolved in xylene to the medicinal oil. The emulsification experiments with ferric hydroxide were not influenced by this addition.

By this method of working, both the oil and the ferric hydroxide were examined in exactly the same medium as that in which they find themselves during emulsification experiments in test tubes.

The cataphoresis measurements were accurate to within ± 3 %. The cataphoresis velocities for the three electrolytes mentioned are given in figure 2. The cataphoresis of the iron hydroxide sol could not, of course, be measured with higher concentrations of electrolyte than the flocculation value of that sol; it was, however, possible to measure the cataphoresis of the medicinal oil in that region. The point of flocculation of the sol is indicated, as also the concentrations at which, in accordance with fig. 1, emulsification just begins and where it is at its optimum [3]).

This diagram shows that the differences in the

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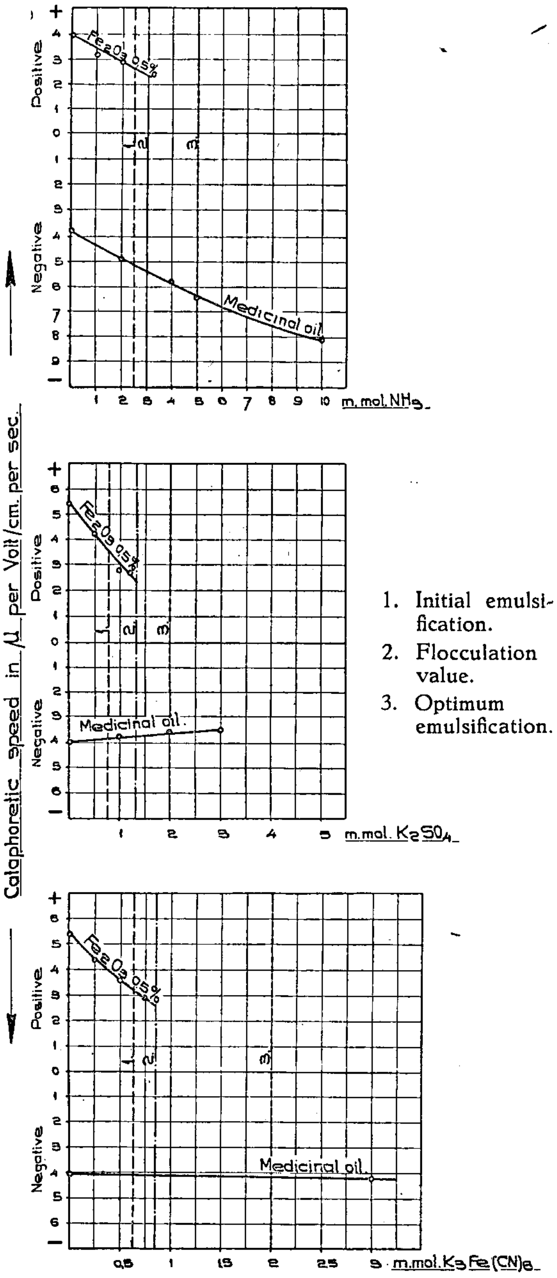
[3]) It should be noted that a different sol was used for the experiments with NH_3 from that employed for the other experiments, a fact which affects the initial value. Its behaviour was the same, however, in emulsification.

charge (electro-kinetic potential) of the oil and the particles of sol show comparatively little change and therefore the chief effect of the influence of electrolytes upon the emulsification must be caused by the flocculation of the sol. In this case of a positive sol like Fe_2O_3, and the oil interface being negative, there will even have been an attractive force; but emulsification does not take place until the iron hydroxide particles have coalesced to a certain extent. It now remains to be seen what it is that brings this about. May be the Brownian movement of the unflocculated particles is too strong for adherence to the interface but, alternatively, it may be that the interfacial film becomes firmer owing to the flocculation, and consequently stabilizes to better effect. Although we have here shown that flocculation may be an important factor in emulsification with colloids, this does not mean that if the oil and the colloid have the same charge, neutralization of these charges will not also influence emulsification.



1. Initial emulsification.
2. Flocculation value.
3. Optimum emulsification.

Cataphoretic speeds of ferric hydroxide and oil of the mixtures of fig. 1.

Finally, let us consider how different hydrocarbons with the same iron hydroxide sol require very different amounts of coagulating electrolyte to emulsify. The experiments were carried out in the same way as those described.

Liquid to be emulsified	Incipient emulsification in m.mol of NH_3 per litre of aqueous phase	Optimum in m.mols of NH_3 per litre of aqueous phase
Xylene	5	7
Medicinal oil . . .	2—3	5
Aromatic-free kerosene hydrocarbons	0—3	9—12
Tetralene	0	5—30
Aromatic-free gasoline, boiling range 60—80° C . . .	Does not emulsify	Does not emulsify

It will be seen that with xylene considerably more coagulating agent has to be added than the amount necessary for flocc. of the sol, whereas with tetrahydronaphthalene emulsification is obtained without the addition of any electrolyte. It is also clear that in this case the quantity of coagulating agent is practically immaterial.

Discussion:

Dr. J. Oosterman asks: What property of a substance makes it act as an emulsifier if it is not its influence on ζ or the surface tension?

In the emulsification of oil by Fe_2O_3 sol the oil particle is covered with Fe_2O_3, so that the oil drop appears as a large particle of Fe_2O_3. At the electrolyte concentration for optimum emulsification the flocculation value of the Fe_2O_3 sol is in some cases far exceeded. Why do not the particles flocculate, and why does the emulsion remain stable.

Dr. van der Minne replied as follows: To recapitulate briefly: A substance is an emulsifier if it has the property of adsorbing at the interface of the two liquids and there forming a layer that prevents the interfaces of two drops of liquid from coming into contact. In some cases ζ has to be of a definite magnitude; in others, it is not necessary that it should. In the latter case — as, for example, with gelatine, — the protective action is brought about by the fact that this colloid, as a lyophilic colloid, can itself continue to exist without an appreciable electrokinetic potential; and in the case of, say, F_2O_3 as stabiliser, it must be assumed that the film formed constitutes an armour, as it were, preventing the oil-water interfaces of two drops from coming into contact. The fact that the Fe_2O_3 is itself flocculated is immaterial to this stabilisation, only sometimes it causes the drops to adhere to each other.

It has, moreover, been found that the amounts of electrolyte needed to flocculate the sol and to cause this adherence between the particles of an emulsion made with this sol are not always the same.

Dr. A. Voet says: Microscopical examination of an emulsion often shows particle adherence without coalescence. In this case it seems as if coalescence is prevented by a mechanical cause, let me call it a "membrane".

This makes it easier to understand, why the

ζ-potential is not the domimant factor in the stability of the emulsions.

Systems with a high potential without "membranes" are instable since the chance of an impact of the particles may be small, but every impact leads to coalescence.

If, on the other hand, "membranes" are present, the potential may be small, but even particle adherence is not followed by coalescence and consequently the system is stable.

According to the lecturer Dr. Voet's remarks are in line with his reply to Dr. Oosterman.

Prof. Freundlich remarks: My own experience with concentrated emulsions has left the impression that the mechanical properties of the layers coating the droplets, their rigidity, elasticity etc. strongly influence the stability and other properties of these emulsions. I would be interested to hear, whether Dr. van der Minne has observed similar fachs.

Dr. van der Minne answers: This undoubtedly is so. Take, for example, an emulsion, the emulsifier of which is clay. It will often be seen that the particles are not round, which points to a certain rigidity of the interfacial film. An emulsion of this kind is well able to withstand mechanical stresses; e.g., it can be stirred with sand to a paste. An emulsion with soap (say potassium oleate) as emulsifier is not proof against such treatment, even if the sand is quite free from electrolytes. The interface cannot resist any pressure and coagulation immediately takes place.

Dr. Muller says: In his introduction Prof. Kruyt said that about six years ago it proved to be necessary to revert in colloid chemistry to the simplest possible systems. Prof. Kruyt chose the silver halogenide sols.

From the papers read by Prof. Rutgers and Dr. Verwey it has, however, become clear that these sols, too, are highly intricate systems, the properties of which lend themselves only to a certain extent to a mathematic treatment.

I therefore wonder whether it would not be desirable also to pay attention to the emulsions when trying to find the simplest possible "model" system. The emulsions prepared with clay and albumens as emulsifier are left out of consideration. I am thinking of the diluted emulsions of pure oils in pure water, studied by Limburg and others, and of emulsions made with "soaps".

What I consider to be the principal advantage of the emulsions is the globular shape of the particles and the consequent homogeneous distribution of the charge over the whole interface. As to the differences between emulsions and hydrophobic sols, such as particle size and origin of the ions on the inner side of the double layer, I believe that these are in degree rather than of a fundamental nature.

When mentioning just now emulsions made with „soaps" I was perfectly aware that with these „soaps" a complicating factor is usually introduced into the system because they are themselves dissolved colloidally, at least not molecularly disperse, in the water phase.

However, in my opinion it might be possible to prepare emulsions with a particle size not differing much from that of the hydrophobic sols (for instance some tenths of microns). This I think might be effected by combining alkyl or aralkylsulphonic acids, which are still molecularly soluble, with a not too strongly hydrophobic oil phase (e.g. an aromatic hydrocarbon or a liquid fatty alcohol). Such a system, with a known composition of the two fases, while the composition of the double layer migh be calculated from experiments, could, to my mind, successfully be employed as a „model" for the study of the hydrophobic dispersion in general.

After Dr. van der Minne: Such "models" certainly have already been studied during research work done by Ellis and Powis, Limburg and others. Colloid chemistry has undoubtedly benefited much by their work, but it has also become apparent that, as a model, these systems are perhaps too simple and do not provide a good model for the study of the problems that arise where various "ordinary" sols are concerned (antagonism of ions, adsorption with flocculation, sensitizing).

This is difficult to explain now, but it may possibly be due to the fact that, unlike the case of the sols, there is here no potential-determining ion, and also to the fact that the particle size of the pure oil-and-water systems is very much larger. For this reason and because of the low disperse phase content, the total interface (e.g. per ml of emulsion) becomes so small that interfacial reactions escape observation. Speaker has himself studied such systems and he is able to say that the experimental difficulties with these model emulsions are very considerable; moreover, several methods of analysis that can be very successfully employed for some of the model sols (such as potentiometry and conductivity with the silver halogenides) cannot be used for them with similar results.

The objection to the use of substances on the boundary line between molecularly soluble ones and colloids, such as soaps, also applies to the sulphonates. If such capillary active substances were used, the properties of the model colloid would be quite repressed. The suggested use of liquid higher alcohols for the oil phase may perhaps be useful. There is just a possibility that, without any further additions, a finer and more concentrated emulsion could be made with them.

Ir. H. Eilers asked to Dr. Hamaker during the present discussion: In connection with the paper read by Dr. van der Minne, I should like to ask whether there is a relationship between the *interfacial tension* on the surface of emulsion particles and the van der Waals—London forces, which, according to Hamaker's theory, cause the coagulation of such systems.

The interfacial tension is considered to be the resultant of the molecular attractions of both phases on the molecules in the interface. One would therefore be inclined to look upon this tension as a measure for the maximum value of the van der Waals-London forces exerted by a particle of the emulsion on a second similar particle. If this hypothesis is correct, the conclusion would be that a low interfacial tension is of direct importance for the stability of emulsion systems.

Dr. Hamaker answers on this question: It is highly desirable to calculate the energy of interaction as a function of the distance between the particles.

As far as I can see such calculations can not be based on the concept of interfacial tension. In two recent papers [1]) I have therefore investigated the London — v. d. Waals attraction without any reference to interfacial tension. I think, hower, that the above question must be answered in the affirmative and that the London — v. d. Waals contribution to interfacial tension is determined by the same constant which fixes the intensity of the attractive forces (the constant A in the paper mentioned). The result that London — v. d. Waals forces always lead to an attraction (see the first paper) then means that these forces always contribute by a positive amount to interfacial tension. Also the magnitude of the interfacial tension will be a direct measure for the intensity of particle attraction, as suggested by Mr. Eilers.

Dr. J. Hoekstra asks: Is anything known about the repulsive and attractive curves as given by Hamaker, at the interface of two fluids?

In Dr. van der Minne's opinion this is not known up to now.

Now Mr. Eilers was called upon by the chairman for delivering the last paper of the Symposium.

Technical application of base materials in emulsified state

by

H. Eilers (Amsterdam).

Introduction.

In the following pages some problems encountered when working up materials in an emulsified form will be dealt with, the examples, being chiefly taken from the application of emulsions of asphaltic bitumens.

In technical literature the term *"emulsion"*, — which in science is restricted to a dispersion of one liquid in another, not miscible with it — is also used for a series of systems whose disperse phase no longer exhibits a true liquid character. Besides emulsions consisting of fatty or mineral oils dispersed in water, it comprises those of very highly viscous materials which exhibit plasticity (such as petroleum asphalt), those of crystallized substances (like paraffin wax, montan wax and crystallized resins), while also latex, the natural dispersion of rubber, may be classed among the emulsions. The technical properties of all these dispersions, however, greatly resemble those of emulsions in the narrower sense of the word.

In the publications [1]) on technical emulsions by Lange and Aladin and in the collection of papers "Technical Aspects of Emulsions", the preparation and application of the various emulsion products is dealt with, whereas Clayton in his wellknown book [2]) devotes more attention to the scientific principles of the emulsification.

With the exception of a few applications of little technical importance, such as emulsions of mercury, one phase of the emulsion is invariably an "oil", either a hydrocarbon oil (e.g. a petroleum product or rubber) or an organic compound of a pronounced hydrocarbon character containing also comparatively small quantities of oxygen (e.g. fatty oils, some waxes and resins) or some other element (e.g. chlorinated products); the other phase is mostly water.

Dispersions of pure "oils" in water are fairly coarse and very unstable: to obtain finer dispersion and greater stability the presence of one or more auxiliary substances is necessary. If this substance is in the first place used to facilitate emulsification, it is called an "emulsifier"; if it is added to an existing dispersion with the object of improving its stability, it is called a stabilizer.

The choice of the emulsifier mainly decides whether an emulsion of oil in water (O/W) or water in oil (W/O) is obtained. The emulsions used for industrial purposes belong, almost without exception, to the former type, though it is often found upon closer examination that its oildrops contain still finer drops of a water phase. The technical properties of such emulsions, however, are mainly determined by those of the oil-in-water system. Therefore in the following the term "emulsions" will be taken to mean emulsion of this type.

As a rule emulsions are used to simplify the working up of a given substance. The choice of the material to be dispersed is governed by the properties desired in the final product. Properties of the base material such as viscosity, brittleness, ductility, stickiness and colour, may be of great importance in this respect. The utilizability of the emulsion during application mainly depends, however, on the emulsifier and the stabilizer chosen.

The title of this article confines its contents to the technical application of materials in emulsified condition. The use of emulsions as food stuffs, pharmaceutical products and cosmetics will therefore not be discussed here, nor can we dwell on the occurrence of objectionable emulsions during some technical processes for instance as they occur in crude oil, or in such cases where they only form an intermediate stage in the normal process of manufacture as in soap making.

Technical uses of emulsions.

When a product, incorporating a hydrophobic base material, is to be prepared, one is often faced with the problem as to how the "oil" may beste be added to the other materials. Must the "oil" be used as such, perhaps after heating to make it more fluid? Must it be incorporated as a solution in a volatile solvent? Or would it be better to employ it in emulsified form?

When answering these questions, it must first of all be kept in mind that emulsions are usually more sensitive materials than oils made utilizable by heating or cutting back. Furthermore the emulsification process requires trained workers, and even these are sometimes faced with unexpected complications due to slight variations in the base materials (for instance the technical emulsifiers).

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[1]) H. C. Hamaker, Physica **10**, (1937); Rec. trav. chim. January 1938.

[1]) O. Lange, Technik der Emulsionen, Berlin, 1924; Aladin, Technisch verwendbare Emulsionen, 1928; Technical Aspects of Emulsions, with a foreword of F. G. Donnan, London, 1935.

[2]) W. Clayton, The Theory of Emulsions and Their Technical Treatment, 3rd ed., London, 1935.

In the following instances, however, it may be preferable to apply the "oil" in an emulsified form:

1. When the material to be incorporated occurs naturally in an emulsified form, as in the case of rubber latex.

In the manufacture of many rubber articles, it is not necessary first to prepare the rubber, but one may immediately start from the latex.

2. When applying "oil" in water-containing mixtures, in which, after the elimination of the water, the "oil" must act as water-repelling agent. Examples are found in the paper industry, where not only rosin size, which may be regarded as an emulsion of resinic acids ³), but also latex ⁴) wax emulsions ⁵) or asphalt emulsions ⁶), are sometimes added to the fibrous material which is dispersed in a large quantity of water, before feeding the stuff to the paper-machine.

Another example is the application of some asphalt emulsions in mixtures with wet sand or cement.

3. When a comparatively small quantity of viscous "oil" is to be distributed over a large surface. An example is found in the textile industry. The textile oils ⁷), applied as highly diluted emulsions of oil in water, permit a uniform spreading of the oil over the fibres, due to the good wetting of the fibre by water and the low viscosity of the emulsion. After the water has evaporated the small quantity of oil is much more uniformly distributed over the extremely large fibrous surface than would be possible without emulsification. Another example is found in the application of asphalt emulsions for surface dressing of roads.

4. When a highly viscous "oil" is to be used in cases where it is impossible to apply heat to make the "oil" sufficiently fluid or to use a volatile fluxing agent.

When a rather fine, porous soil has to be impermeabilized with an asphaltic bitumen in great depth it is impossible to apply molten bitumen as it would cool down too rapidly to secure satisfactory penetration. A cutback is also unsuitable as evaporation of the solvent is not possible. The Shellperm-process ⁸) gives a solution of this problem by injecting the soil with a bitumen emulsion. After the coagulation of the emulsion in situ an asphalt-sand mass still containing water in the closed pores is obtained, which is practically impermeable to water.

5. When, by using emulsions, a final product with special properties can be obtained.

This is exemplified by the use of asphalt emulsions, containing a solid substance as emulsifier ⁹), as paint. Upon evaporation, the emulsifier (only a low percentage of the weight of the asphalt) forms a spongey skeleton impeding, even at high temperatures, the flow of the soft asphalt by gravity.

6. When the large total surface of the emulsified "oil" can be used to facilitate absorption in the "oil"-phase, or to promote chemical reactions.

Examples of this application of oil in the emulsified form are provided by a process in which the oxidation of linseed oil to linoxyn is carried out after emulsification of the linseed oil ¹⁰), and by the vulcanisation of rubber latex.

Another application of this principle is the intravenous injection of oil emulsions as absorbants for poisons separated by bacteria in blood ¹¹).

7. When the electric charge of the colloidal particles can be used, as is done in electro-deposition of rubber latex. The negatively charged rubber particles are deposited on the conducting surface of the anode. Secundary reactions, particularly evolution of gas due to electrolysis, may cause porosity of the deposited rubber. It is stated ¹²) that when using a rubber dispersion with particles, whose electric charge is reversed by strong acidification, and which are deposited on the kathode, a better product is obtained.

Another application of electro-deposition of emulsion particles is said to be made in the Eric ¹³) process for internal painting of water mains in situ with asphalt, precipitated on the walls from an emulsion by electric current.

In some cases it is stated that the adhesion of "oil" separated from emulsions is much better than that of "oil" applied to the material by impregnation. Compounds of soaps from the emulsion with polyvalent positive groups, present or absorbed in the material, should then constitute a transition layer promoting the adhesion of the "oily" matter to the base.

Lorenz ¹⁴) states that the resistance of paper to writing ink is considerably better when the rosin particles are precipitated onto the paper fibre with the aid of alum sulphate than when the precipitation is effected with sulphuric acid or when the paper is sized by impregnation with a rosin solution.

The "fat liquoring" of chrome leather ¹⁵), is probably to be considered as a similar fixation of "oil" to a hydrophylic material by means of metal salts. In this process the leather, which has a weak acid reaction and contains complex chrome compounds, is treated with an oil emulsion and tenaciously retains the grease separated from it.

Emulsifying agents and processes.

A discussion and classification of the different substances that can be used as emulsifiers in general has been given in the paper read by van der Minne. Here only an example of technical emulsification will be dealt with in detail.

Nearly all the different procedures in which *asphaltic bitumens* are technically emulsified by

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³) R. Sutermeister, Tech. Assoc. Papers, Series XIX, 460 (1936); H. N. Lee, Paper Trade J. **103**, 386 (1936).

⁴) M. Dériběré, Papier **39**, 775 (1936).

⁵) R. W. Kumler, Paper Trade J. **104**, 154 (1937).

⁶) Belani, Bitumen **3**, 120 (1933); F. Hoyer, Papier-Fabr. **34**, 275 (1936).

⁷) J. B. Speakman, J. Soc. Chem. Ind. **53**, 173 T (1934).

⁸) J. v. Hulst, Ingenieur **50**, B 66 (1935).

⁹) J. Göbel, Ingenieur **50**, Mk 8 (1935).

¹⁰) P. C. v. d. Willigen, Verfkroniek **9**, 16 (1936); Ned. Octr. 17975, 22635.

¹¹) V. G. Walsh & A. C. Fraser, Techn. Aspects, page 5 (see note 1).

¹²) H. P. Stevens & W. H. Stevens, Techn. Aspects, page 129 (see note 1).

¹³) S. A. M. Williams, Can. Eng. **66**, 19 (1934).

¹⁴) N. Lorenz, in J. Alexander, Colloid Chemistry IV, 85 (1932).

¹⁵) W. R. Atkin and F. C. Thompson, Techn. Aspects, page 119 (see note 1).

means of *soaps* may be divided into two main groups *).

a. the bitumen, heated to such a temperature (say 110° C.) that is it comparatively thin fluid is very intensively mixed with a soap solution. Working on these lines, a sufficiently fine and evenly dispersed emulsion of 50—60 % concentration can, generally speaking, only be obtained when the phases are mixed in a very powerful mixing apparatus, e.g. in a colloid mill. The particle size of these dispersions is mainly determined by the construction of the apparatus 16). With the mills used in such plants and with a suitable soap solution evenly dispersed emulsions with an average particle size of from 2.0—3.5 μ may in this way be prepared.

The chemical stability of these emulsions is mainly determined by the composition of the soap solution, which generally contains a small quantity of free alkali. We would call this mode of emulsification, in which the division of the oil phase is brought about by mechanical force, *mechanical emulsification* (cf. „Mechano-chemistry" 17)).

b. A more interesting procedure from a chemical point of view is that in which an "oil", which contains a hydrocarbon-chain acid, is dispersed in dilute lye. The soap formation assists the emulsification, so that — given appropriate emulsification directions — even with moderate stirring a fine and uniform dispersion may be obtained (see v. d. Minne's paper). We would call this mode of emulsification: *chemical emulsification.*

Some asphaltic bitumens contain by nature enough organic acids in order that finely dispersed emulsions can be produced by mixing the molten bitumen with dilute alkalies. Other asphaltic bitumens require the addition of larger or smaller quantities of hydrocarbon-chain acids before emulsification.

Chemical emulsification is only possible when the interfacial tension in the system oil/water is very low. Traxler and Pittman 18) carried out measurements on the interfacial tensions in the system asphalt/electrolyte solution with the tensiometer of Lecomte du Noüy at 85° C. In these experiments two asphalts were used: Flux A from Venezuelan origin, and flux B from Trinidad crude. A few data taken from these publications are given in table I.

Table I.

Interfacial tension of two bitumens against solutions of sodiumhydroxyde of different concentration (Traxler and Pittman).

Conc. NaOH mol/l	Flux A	Flux B
0.000	16.7	15.7
0.0013	11.4	7.9
0.0025	9.5	5.3
0.0050	5.3	0.0
0.010	0.5	0.0
0.05	0.0	0.0

The interfacial tension between these bitumens and the very dilute alkali solutions decreases with increasing alkali concentration. The authors remark that spontaneous emulsification occurred in those experiments, in which they found the value 0 for the interfacial tension.

To sodiumhydroxyde solutions whose interfacial tension against these bitumens was 5 dynes/cm (underlined values in Table I), increasing quantities of sodium chloride were added. Figure 1 gives the values for the interfacial tensions, found by Traxler and Pittman, plotted against the chloride concentration.

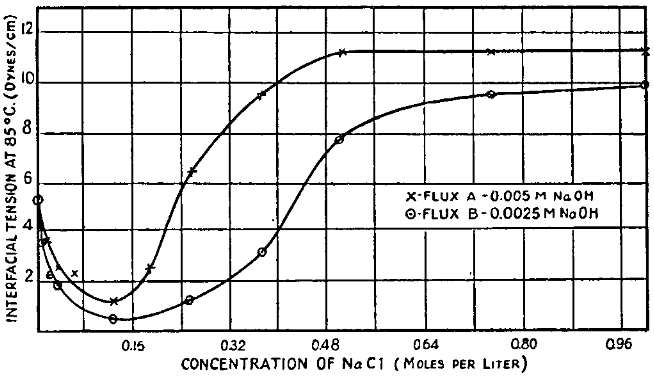

Fig. 1. Effect of sodium chloride on interfacial tension. (Traxler and Pittman).

From these experiments it follows that the addition of a small quantity of sodium chloride to a sodium hydroxyde solution too dilute to produce a very low interfacial tension against these bitumens, causes a decrease in interfacial tension, but that larger quantities of sodium chloride cause a considerable increase, probably due to salting out of the soap.

In a further series of tests they determined the interfacial tension against solutions of different neutral and weakly alkaline sodium salts as a function of the pH-value. Fig. 2 shows the results obtained with flux A.

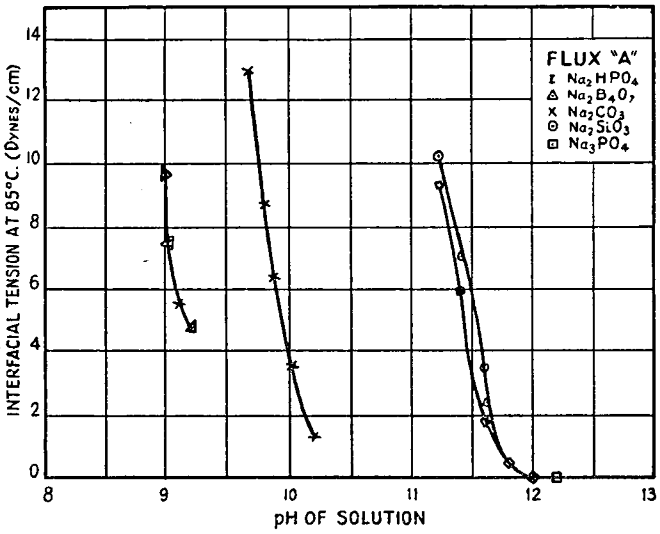

Fig. 2. Interfacial tension of flux A against various electrolytes plotted as function of the pH of the solution. Traxler and Pittman).

These tests give the impression that the interfacial tension mineral oil/electrolyte solution in the case of asphaltic bitumens is determined by the anion in a

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*) Some procedures, which are probably to be considered as applications of *"spontaneous emulsification"*, will be left out of discussion.

16) R. I. Johnson gives in Technical Aspects, page 44, a description of various mills (see note 1).

17) P. M. Travis, Mechano Chemistry and the Colloid Mill, New York (1928).

18) R. N. Traxler & C. U. Pittman, Ind. Eng. Chem. 24, 1003, 1391 (1932).

higher degree than appeared from the tests by Weiss and Vellinger[19]). The latter found, with respect to refined lubricating oil distillates, a slight influence of the anion and a marked effect of the pH value.

In fig. 3 we have plotted the average diameter of the particles of 60 % emulsions from a Venezuelan bitumen[20]) emulsified in a standardized way in alkali solutions of different concentrations.

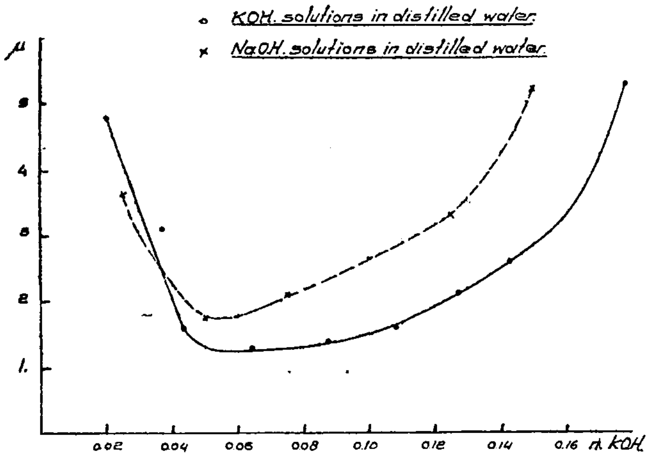

Fig. 3. Average diameter of particles of emulsions ex Venezuelan bitumen in dilute solutions of NaOH and KOH of different concentrations.

Emulsification in very dilute alkalies produces coarse emulsions. In more concentrated caustic solutions the average particle size of the emulsion decreases, to increase rather markedly in still more concentrated solutions. While the decrease may be associated with the lower interfacial tension of the bitumen against somewhat more concentrated lyes, the increase in particle size at still higher lye concentrations may most probably be accounted for by salting-out. This susceptibility to higher electrolyte concentrations is often more pronounced when using caustic soda than when caustic potash is used. When other bitumens, and bitumens to which soap forming acids have been added, are emulsified, a similar dependence of the particle size on the concentration of the lye will be noticed. However, in a large number of cases the optimum emulsibility will be found at a somewhat higher alkali concentration.

The tests made by Traxler and Pittman (fig. 1) showed that addition of alkali-chloride may as well increase as decrease the interfacial tension against oil. In fig. 4 the average diameters of the particles are given of 60 % emulsions from Venezuelan bitumen in potassium hydroxyde solutions. These were made in distilled water as well as in water containing a small quantity (0.20 %) of potassium chloride.

At low lye concentrations the addition of salt improves the emulsification, but in higher concentrations it increases the salting out effect.

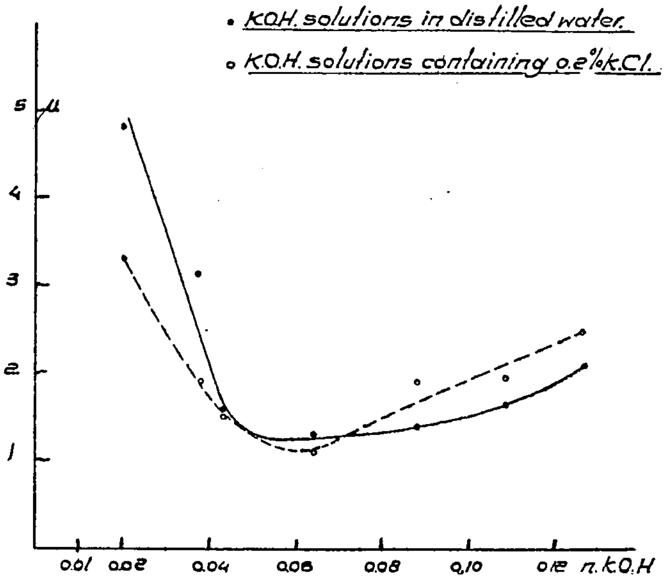

Fig. 4. Average diameter of particles of emulsions from Venezuelan bitumen made with potassium hydroxyde solutions in distilled water and in water containing 0.2 % of potassium chloride.

The difference in minimum particle size that can be obtained with potassium hydroxyde and sodium hydroxyde, and the influence of chlorides on emulsification, show that the effect of the chemical emulsification process depends on various factors, among which the pH value. However, to this magnitude should not be assigned so predominant an influence as done by Vellinger and Radulescu[21]) when they sum up their results in: "The degree of dispersion of bituminous emulsions varies with the pH of the aqueous phase".

Viscosity of emulsions.

There is no general equation by which the viscosity both of dilute and highly concentrated emulsions can be indicated. For technically uniformly disperse, well-peptized emulsions of a concentration at which the volume of the disperse phase is 50—70 % of the total volume, we may apply the equation of Hatschek-Sibree[22]):

$$\eta' = \frac{\eta}{1 - \sqrt[3]{k\varphi}}$$

η' = viscosity of the emulsion; η = viscosity of the continuous phase; $\varphi = \text{ratio} \; \frac{\text{volume of spheres}}{\text{total volume}}$

k = a constant.

The viscosity of such a system does not depend on the viscosity of the disperse phase: the equation can be used both for emulsions of paraffin oil and of asphalt. The factor k is for many technical emulsions 1.3—1.4; it is affected by the particle size/frequency curve: by mixing a coarsely dispersed system with a more finely dispersed system, emulsions can be obtained with considerably lower viscosity than would be expected. When applying this equation it must also be borne in mind that the volume of the particles of an emulsion is in many

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[19]) H. Weiss & E. Vellinger, Compt. rend. 188, 901 1099 (1929).

[20]) It cannot be ascertained to what extent the bitumen used (which, without the addition of emulsifier acid, produces finely dispersed emulsions in dilute lye) is comparable with the flux A examined by Traxler and Pittman. The characteristics of our bitumen were pen/25° C : 180—200; mpt. R. & B. 39° C.

[21]) E. Vellinger & G. Radulesco, Preprint World Petroleum Congr., Paris, 1937.

[22]) Sibree, Trans. Faraday Soc. 26, 26 (1930); 27, 161 (1931).

cases larger than the volume of the dispersed oil, as often the particles of the oil phase enclose drops of water that increase the volume of the disperse phase[23]).

Equations can only be applied to those emulsions of which it must be assumed that the repulsive electrical forces between the emulsion particles are sufficient to prevent cohesion between them. In the case of other emulsions, for instance those that are made with the aid of slightly flocculated solids, these equations may not be used. Their rheological behaviour (plasticity, thixotropy) is too complicated to be mathematically treated. The plastic properties of such a system can moreover be partly due to the irregular shape of the particles, which produces abnormal resistance to flow.

Stability of emulsions.

The various applications of emulsions make highly divergent demands on the stability of the system. It is generally required that an emulsion, before application, should remain stable under storage, i.e. show little sedimentation or creaming and no material increase of the percentage of coarse matter in course of time or under fairly great temperature fluctuations, often below freezing point. Further the emulsion should withstand the manupulations during application, i.e. it should be sprayable, allow of being mixed with other materials or withstand the mechanical friction of pumps and other machine parts without coagulating. These demands might induce manufacturers to prepare a very stable type of emulsion, for instance, by using large quantities of emulsifier.

A very stable emulsion will, however, not always be satisfactory, as, besides the desired stability mentioned above, the system should in many cases coagulate rapidly and irreversibly after application. For instance, a bitumen emulsion sprayed on a road should, within a fairly short time, form a coherent coat of bitumen adhering to the stones, while a paint with an emulsified oil as binder, may not show reemulsification when, after drying, it comes into contact with water.

In order to meet these conflicting demands the emulsification directions should be carefully drawn up. By selecting emulsifying agent and procedure a compromise should be made between the different demands.

As stated above a factor of great importance for the stability of the emulsion during storage is its resistance to sedimentation. This factor is not only dependent on the choice of emulsifier solution, but also on the fineness of the dispersion. The choice of the emulsifier solution governs the electric charge repelling the particles and promoting their homogeneous distribution in the medium. The fineness of the dispersion determines the velocity of sedimentation in dilute emulsions, which according to Stokes' law is proportional to the square of the radius of the particle. In concentrate systems this law is no longer valid, but will still give a qualitative description of the differences that may occur.

When subjected to mechanical treatment, other properties of the emulsion determine its resistance, e.g. the consistency of its disperse phase. During the technical applications of emulsions, the system will be subjected to various cooperating influences leading to its coagulation.

The reactivity of the emulsifying agent mainly determines the stability against chemical influences, of the emulsion prepared with it. In general an emulsion will coagulate if a reaction between the soap emulsifier and a substance with which it is brought into contact produces an insoluble product. In most cases the emulsifier (soaps of technical waste products like liquid rosin, low grade colophony or sulphonic acids formed during the purification of mineral oils), as well as the substances with which the emuslsion comes in contact (e.g. stones, pigments) are chemically not sharply defined.

The first experiments applied to study the technical stability will have to be a close imitation of technical conditions. To obtain a correct idea of the process, it will be necessary to analyse what actually happens in practice, frequently to split the total phenomenon into the various simultaneous processes, and to study the behaviour of the emulsions in each of these separately. To judge the emulsions, basing one's opinion on only one of these processes, may lead to erroneous conclusions.

The great diversity of uses to which emulsions are put makes it impossible here to deal with problems of technical stability completely. We shall only discuss some technical examples of the application of emulsion more in detail.

1. An apparently simple application of an "unstable" emulsion is the surface dressing of road carpets with asphalt emulsions[24]). On the road carpet a thin layer of a 50—60 % asphalt emulsion made with a soap as emulsifier is poured or sprayed and then chippings are strewn on to the road. After a moderate interval the emulsion must coagulate and form a cohesive layer adhering well to the road underneath and to the chippings. As such emulsions should coagulate fairly rapidly, the emulsions chosen for this purpose must not be too stable. Yet such a product, which is often manufactured in a plant at a considerable distance from the place where it is to be used, must be capable of resisting fairly long storage and conveyance over long distances at varying temperatures.

The emulsion must also be sufficiently stable to be uniformly spread over the surface of the road with brooms (squeegees) or some similar implement immediately after it is poured on to it, while its consistency must be sufficient thick to prevent its flowing from a slightly cambered road in the time elapsing until the chippings have been spread on the road and coagulation starts. This can be due to various cooperating factors:

1. Reaction between the road underneath, the stone and the emulsion, while also absorption of carbondioxide from the air or loss of volatile emulsifiers (ammonia) may play a part;
2. Withdrawal of water by filtration into the soil and by evaporation;
3. Mechanical forces: rolling and traffic.

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[23]) L. G. Gabriel, Techn. Aspects, pag. 140 (See note 1).

[24]) F. H. Garner, L. G. Gabriel & H. J. Prentice, Modern Road Emulsions, London, 1933.

As a first criterion for the breaking of the emulsion its change in colour from chocolate brown to black can be taken. The first thorough investigation into the influence of the stones on the breaking of the emulsion was made by Weber and Bechler[25]). They immersed the stones in question, a narrow sieve fraction of the technical material, for some time in the emulsion to be tested, then the emulsion was poured off, the stones rinsed and dried. The increase in weight in percent of the weight of the stone gives the coagulation value or "Zerfallswert".

With one kind of stone in one granular size, coagulation is practically proportionate to the quantity of stone, and with different grading it is more complete as the total surface of stone is larger.

In Table II some data are given relating to the behaviour of an unstable emulsion in contact with various stones.

Table II.

Coagulation of an unstable emulsion, expressed as the "Zerfallswert" (coagulation value), by contact with various kinds of stone for 1 hour and 48 hours (taken from Weber and Bechler).

Coagulation at the end of	1 hour	48 hours	48 hours / 1 hour
Porphyry (Dohna)	5.8	42.8	7.9
Limestone (Beilngries)	4.1	21.1	5.2
Diabase	1.3	6.7	5.2
Syenite	0.9	6.8	7.5
Furnace slag	0.8	3.0	3.8
Basalt	0.5	0.5	1.0
Limestone (Herrlingen)	0.5	0.5	1.0

Coagulation in contact with different kinds of stone proceeds at different rates. If coagulation is slow at the start, it continues slowly, or stops altogether, whereas, if a large quantity of coagulum is formed during the first hour, it continues fairly rapidly.

The stones that produce little coagulum in the test of Table II do not give much coagulate with any emulsion. Other, more stable emulsions do not coagulate to any extent with any of the stones (see table III).

The differences in the quantity of coagulum formed by one emulsion in contact with different kinds of stone are also observed with all other corresponding gradings of these materials.

Table III.

Relation between the acid reaction of the stone and the coagulation of emulsion in contact with it.
(Taken from Klinkmann).

	Limestone	Diabase	Basalt
Loss of NaOH in gms. *)	8.9	11.1	30.5/31.6
Coagulation values:			
stable emulsion	0	0	0
slowly coagulating emulsion	0	0	9.1
rapidly coagulating emulsion	3.5	5.5	19.8
labile emulsion	33.3	34.0	97

*) 30 ml of stone was put away with 60 ml of 0.2 % NaOH solution. 25 ml of the liquid was titrated.

From the investigations carried out by Weber and Bechler and by Klinkmann[26]) it follows that the stones bind alkali and that in general as a stone binds more alkali it has a stronger coagulating effect on the emulsion, as is shown in tables III and IV.

If such stones are previously washed with dilute alkali even an unstable emulsion does not form a coagulum in contact with these stones. Emulsions containing little free alkali are less stable to this coagulating influence of the stone than emulsion with more free alkali (compare emulsions 2—4 and 3—6 of table IV and fig. 5). This graph shows that the coagulation of the emulsions 2 and 3 with low alkali content is practically proportionate to the alkali fixation of the stones with which they are in contact.

The stones not only bind alkali, but also fatty acids from soap solution, with which they are in contact. In most cases the absorption of acid substances is not so marked as that of alkalies. Klinkmann, however, observed that a phorphyry from Bolzano, which did not absorb much alkali, still had a strong coagulating action on the emulsion; this was due to the fixation of part of the soaps of the emulsifier solution by the stones.

Keppeler, Blankenstein and Borchers[27]) examined the binding of lye, of basic- and of acid-dyestuffs by these stones (table IV), and compared these values with the coagulating action they have on unstable emulsion. With an emulsion containing only a small amount of alkali the coagulation was found to be proportional to the binding of alkali by the stone.

Table IV.

Absorption of alkali and dyestuffs by stones in connection with their coagulating effect on emulsion. (Taken from Keppeler, Blankenstein and Borchers).

Stone	KOH absorbed per 10 g of stone	Methylene blue absorbed	Congo red absorbed	Asphalt coagulated per 100 gm of stone from emulsions made with				
				2 0.2 % KOH 1.0 % oleic acid	3 0.2 % KOH 2.4 % oleic acid	4 1.0 % KOH 0.2 % oleic acid	5 1.0 % KOH 1.0 % oleic acid	6 1.0 % KOH 2.4 % oleic acid
Petersberg porphyry	23.0	0.22	0.030	30.7	16.8	20.2	10.1	1.6
Basalt III	21.2	0.21	0.023	28.5	16.8	16.3	8.3	0.7
„ O II	15.1	0.155	0.012	20.2	11.2	9.6	3.9	0.4
„ O I	14.7	0.155	0.011	19.3	9.0	9.2	2.3	0.5
Schaumburg Limestone	4.5	0.055	0 055	6.9	1.9	0.8	0.8	0.4
Hasselrode granite	0.8	0.018	0·009	0.3	0.2	0.1	0.1	0.1
Mansfeld copper slag	0.11	0.01	0.01	0.4	0.2	0.1	0.1	0.1

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[25]) H. Weber & H. Bechler, Asphalt und Teer **32**, (1932), a series of articles.

[26]) G. H. Klinkmann, Asphalt und Teer **33** (1933), a series of articles; G. H. Klinkmann, Bitumen **5**, 206 (1935).

[27]) G. Keppeler, P. Blankenstein and H. Borchers, Z. angew. Chem. **47**, 223 (1934).

As the degree of coagulation is not only dependent on the nature and origin of the stone, but also on possible weathering after it has been quarried ("Bergfrische"), it is extremely difficult to prescribe official methods for testing emulsions, based on coagulation in contact with stone.

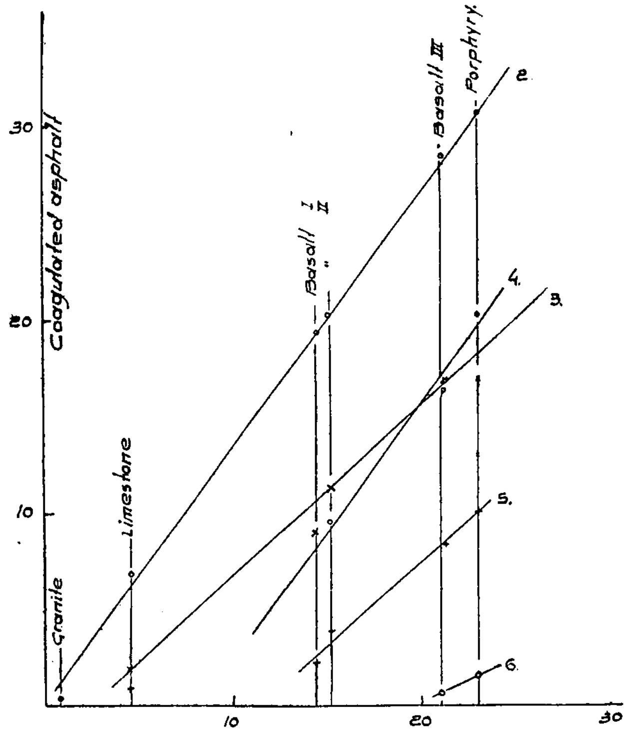

Fig. 5. Relation between alkali fixation by stone and coagulation of emulsions (Taken from Keppeler, Blankenstein and Borchers).

The amount of coagulate formed in an emulsion in contact with stone is moreover influenced by the temperature; as Klinkmann observed (Table V) it increases considerably with the temperature.

Table V.

The influence of the temperature on the coagulation of an emulsion in contact with limestone (Klinkmann).

Temperature	Coagulation value
6°.5 C	1.4
11 „	3.5
16 „	6.2
23 „	10.2

These reactions between the stone and the emulsion will principally occur during the first period after spreading on the road. As a result of this chemical coagulation the stones can be coated by a fairly impermeable film that prevents further reaction. Further coagulation, and, if not very reactive stones are used, practically the entire coagulation, will have to be effected by other influences. Thus, the absorption of carbon dioxde by the emulsion spread out in a thin layer over the road may promote breaking, but the chief factor will certainly be the evaporation of the water. The rate of evaporation depends on atmospheric conditions: the temperature, humidity and motion of the air. Under similar atmospheric conditions it is, at least at first, approximately equal for the various emulsions. But the water content at which coagulation occurs varies. A method of differentiating between the various emulsions based on this difference is the "Lability Test" [28].

In this test the emulsion is concentrated under specified conditions in a current of air, of constant temperature and free of carbon dioxide; the water content of the emulsion when 66 % of the bituminous material has been coagulated, gives a measure for its stability.

The coagulation can be accelerated by capillary water absorption in the foundation.

It will now be clear that considering the complicated nature of the coagulation process, a measurement of the stability based on a simple test in which the emulsion is mixed with an electrolyte solution (e.g. the Myers Test [29]) with calcium chloride) can only give a very one-sided and unreliable idea of the technical properties of an emulsion, and that it must be endeavoured to make the analytical method as close an imitation of actual conditions as possible.

2. When it is desired to use an emulsion for composing a mixture containing a large amount of solid substances a more *stable emulsion* must be used.

In the previous section it was shown that even coarse stones can coagulate considerable quantities of emulsion, and that their reactivity increases with their fineness. In most cases where it is desired to mix an emulsion with a great quantity of finely divided inorganic material, e.g. when mixing rubber emulsions with fillers, or making mixes of asphalt emulsion with cement or the like, the reactivity of the filler makes it impossible to use emulsions prepared with a soap, unless it contains so great a quantity of soap or free alkali that other properties of the mixture would be damaged.

More stable emulsions, more suitable for this type of work, are those with a colloidal *polymeric organic substance*, e.g. a protein, as emulsifier. This form of emulsion occurs in nature in the form of milk and of latex, but can also be produced artificially, for instance by emulsifying an asphaltic bitumen in a casein solution.

The chemical stability of emulsions with similar emulsifiers will be principally dependent on the reactivity of the protein. Emulsions with casein will, like this substance, be reather insensitive to contact with metal salts, but coagulate when acidified up to a pH of about 4.5.

A typical example of this type of emulsions is latex [30]). Though the structure of the latex particle has not yet been fully established, it may be considered as being built up of a rubber nucleus surrounded by a rigid absorption film, which is responsible for the occurrence of non-globular particles. This absorption layer, which, besides proteins, probably contains fatty acid soaps and lecithin derivatives, flocculates if acidified up to a p_H characteristic of the stabilizing agent.

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[28]) J. F. T. Blott & A. Osborn, Asphalt und Teer **34**, 817, 829 (1934); British Standard Spec. 434.

[29]) R. Smith, Ind. Eng. Chem., Anal. Ed. **4**, 105 (1934).

[30]) A. v. Rossem in J. Alexander, Colloid Chemistry IV, page 235 (1932).

In a flocculated latex the rubber particles are still separated by the absorption films. In order to obtain a coherent rubber mass it is necessary that the rubber of the different particles unites, i.e. that coalescence occurs. This coalescence is probably brought about by an enzyme, the coalase 31), or by the presence of a thermo-stable surface-active substance 32), e.g. a kind of cholesterol.

When emulsions of this type are brought in contact with finely divided powders, such as pigments, fillers and the like, sometimes flocculation and coagulation can occur, due to the fact that the large surface of these substances adsorbs the protective colloid of the emulsion, thereby decreasing its stability. This tendency to adsorb proteins of the casein type is much stronger in a neutral medium ($pH = 7$) than in a weakly alkaline medium ($pH = 9$), so that in some cases the addition of a small quantity of alkali to the filler, in others saturation of the filler with the protein before the mixing with emulsion, can solve the difficulties.

The presence of proteins in these emulsions make them vulnerable to bacteriological action leading to their decomposition. Besides special preservatives also a high alkalinity impedes the development of these micro-organisms. Still, one has to be careful when increasing the pH of these emulsions, as the proteins themselves are hydrolyzed in a pronounced alkaline medium. The stability of such emulsions will decrease on storage (e.g. latex, preserved with ammonia).

In some cases, e.g. for mixing with solids carrying a positive electric charge these emulsions are not suitable either, but emulsions whose particles have a positive charge themselves must be used. When latex 33) is acidified to a pH value of 3.5—1.0 a rather stable system with particles having a positive charge is obtained, but better results can be obtained when this reversal of charge is the result of the adsorption of polyvalent kations, e.g. alumium ions, by the particle of the emulsion, especially so when the mixing is carried out rapidly in the presence of a protecting colloid, so that during the passing from one stable system to the other practically no coagulation can occur 34).

The most stable emulsions are made with finely divided inert powders e.g. clay. When such an emulsion is mixed with various substances and worked up only a short time afterwards, only some slight variations in the rheological properties of the system due to differences in the flocculation of the emulsifier can occur. In the long run, however, these clays may show an exchange of ions 35) on prolonged contact with electrolytes. Bentonite, a "sodium clay", may in a weakly acid medium exchange sodium for hydrogen; or in a medium with calcium salts, be converted to a calcium clay. In this way the bentonite becomes more oleophylic and hence better wettable by the oil phase.

As the rheologic properties of such emulsions are influenced by flocculation, the viscous and plastic behaviour may vary due to similar exchange of bases.

Discussion:

Dr. H. L. Bredée inquires whether there is a possible explanation of the so-called "Totmahleffekt". which is observed under certain conditions, when a very fine emulsion is kept in motion mechanically for some time after its preparation, whereby an increase in particle-size takes place. Does there exist an influence of the emulsifier on this phenomenon, which in practise is often found to be undesirable?

Dr. Limburg remarked to this question that the coagulating effect of mechanical action (stirring, vibrations, etc.) is well known. At least a part of this effect can be explained by the increase of the number of collisions between the particles with a given kinetic energy. Smoluchowsky 36) calculated this effect to be, in first approximation, proportional to the third power of the diameter of the particles.

Dr. R. Houwink asks: Is there any special reason why no more modern formulas for the viscosity-concentration function have been applied. It seems very interesting to investigate whether the formulas (26), (27) and (28) developed in Kolloid-Z. 37) will also hold for asphalt emulsions and whether the theoretic considerations as to the influence of particle shape of dispersed particles will be found confirmed.

Ir. Eilers answers that equations for the viscosity-concentration relationship can only be checked with those emulsions which do not show plasticity or thixotropy, that is with emulsions with well peptised particles, e.g. emulsions with soaps as emulsifier. These emulsions have always spherical particles. Emulsions with more irregulary shaped particles, e.g. those with clay as emulsifier, cannot be used for these determinations, on account of their flocculated state, which is the cause of a marked degree of plasticity and thixotropy. When peptizing these emulsions with dilute alkali the particles assume a spherical shape.

The volume calculated for the viscosity of concentrated emulsions with the formula of Bredée and de Booys (No. 26) applied for spherical-non-solvated particles, are very close to those obtained by the older formula of Hatschek-Sibree. The new formula (26):

$$\eta' = \eta \left\{ 1 + \frac{2.5\,\varphi}{6\,(1-\varphi)} \right\}^6$$

(for meaning of the symbols see section on "viscosity of emulsions" of this article) seems to have the advantage, that it can perhaps also be used for more dilute systems. Which of the two equations gives the closest approximation must still be investigated.

The other formulae 27 and 28 in the articles in "Kolloid-Zeitschrift" give, on calculation on the same assumption, too low values for the viscosity.

Now the Symposium was closed by the chairman with a vote of thanks devoted to all who contributed to this succesfull-meeting.

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31) O. de Vries & N. Beumée Nieuwland, Archief v. Rubbercultuur **8—13** (1924—29).

32) N. H. v. Harpen, Rubbercultuur **13**, 1 (1924).

33) G. S. Whitby, Plantation Rubber, 1920.

34) Ned. Octrooi 23147.

35) R. M. Woodman & McKenzie Taylor, J. Phys. Chem. **34**, 299 (1930).

36) Z. physik Chem. **92**, 155 (1918).

37) Kolloid-Z. **29**, 31, and 138 (1937).

BOEKAANKONDIGINGEN.

544.83

Gerhard Kramer, Mikroanalytische Nachweise anorganischer Ionen. Ausführung und Reaktionsbilder. Mit einem Vorwort von Wilhelm Böttger, Leipzig, Akademische Verlagsgesellschaft m.b.H., 1937, 35 pp. und 8 Tafeln, 16 × 23 cm, RM. 5.60 (kart.).

Het kwam eens voor, dat men van eenige metaalionen kleine hoeveelheden had op te sporen en men kwam tot de ontdekking, dat de microchemische kristalreacties daartoe zeer goede diensten kunnen bewijzen. In zulk een geval kan men dankbaar de daarover geschreven publicaties aanvaarden en het misschien alleen betreuren, dat men zich daarvan niet eerder op de hoogte heeft gesteld. Maar men kan in dat geval ook eenige foto's van goed geslaagde reacties maken en er zelf een boekje over schrijven. Dit laatste heeft Gerhard Kramer gedaan.

Er komt in zijn boekje weinig oorspronkelijks voor; het belangrijkste is de aantooning van Cl'-, Br'- en J'-ionen naast elkaar met platinasulfaat, hetgeen door Kramer onlangs ook gepubliceerd is in het Zeitschrift für analytische Chemie. Overigens zijn de reacties nagenoeg alle tot in bijzonderheden ontleend aan Behrens' „Mikrochemische Analyse" en aan Schoorl's „Beiträge".

Het is alleen te verwonderen, dat Prof. Böttger een aanbeveling voor dit boekje schreef en dat de prijs zoo hoog is.

N. Schoorl.

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662.62(022)

Symposium on Industrial Fuels. A.S.T.M. publication, Philadelphia, Pa., 1936 15 × 23 cm, 70 pp., 75 dollarcents.

Het boekje bevat de volgende lezingen: A. C. Fieldner and W. A. Selvig, Coal and coke, 28 pp., 10 fig., 5 tab.; H. V. Hume, Industrial fuel oils, 16 pp., 1 tabel; P. T. Dashiell and F. H. Trembly Jr.; Manufactured gas, 14 pp., 1 tabel; W. H. Bateman, Liquefied petroleum gas, 10 pp.

Deze voordrachten geven een algemeen overzicht van de behandelde onderwerpen. De inhoud omvat een historisch overzicht, de beteekenis der industrie, voorraden, mogelijk nieuwe procédé's, methoden van onderzoek, waarde dezer methoden, toepassing der brandstoffen en algemeene economische vooruitzichten.

D. J. W. Kreulen.

* * *

543.8 : 553.94(42)

The Coal-Seams of North Staffordshire, No. 39, published by the Phys. and Chem. Survey of the National Coal Resources; 15 × 24 cm, 49 pp., 9 tabellen, uitslaande kaart en plaat. H. M. Stationery Office, 1937, 1 s. 6 d.

Een uitvoerige beschrijving van acht opeenvolgende koollagen. De monsters werden op verschillende plaatsen door het geheele gebied getrokken en onderzocht op cokesvormende eigenschappen, water, asch, vluchtige stoffen, zwavel, elementaire analyse, calorische waarde en smeltverloop der asch. De uitslaande plaat geeft de kooksen verkregen bij de laboratoriumdestillatie volgens Gray-King.

D. J. W. Kreulen.

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543.8 : 553.94(42)

The Yorkshire, Nottinghamshire and Derbyshire Coalfield. Analysis of Commercial Grades of Coal, Part 1, No. 37, published by the Phys. and Chem. Survey of the National Coal Resources; 15 × 24 cm, 141 pp., uitslaande plaat en afbeelding. H. M. Stationery Office, 1937, 2 s. 6 d.

Het boek is uitgegeven in den vorm van een tabellenboek. Van 29 verschillende mijnen worden de produkten, die afzonderlijk worden afgeleverd, vermeld met de analyse. De analyse omvat: water, asch, vluchtige stoffen, aschkleur, cokeskarakter, afmeting der bij de bepaling van het percentage vluchtige stoffen verkregen cokes, zwavel, fosfor, chloor, calorische waarde, aschsmeltverloop zoowel in oxydeerende als in reduceerende atmosfeer (reduceerend bedoeld als halfreduceerend), elementairanalyse en opbrengst aan cokes, teer, vloeistof en gas bij de destillatie volgens Gray-King (600° C.).

D. J. W. Kreulen.

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661.97(022)

E. L. Quinn and Ch. L. Jones, Carbon Dioxide. Reinhold Publishing Corporation, New York, 1936, 294 pp., geb. $ 7.50.

Een van de bekende monografiën van de American Chemical Society. In dit werk wordt een zeer ruim overzicht gegeven over alles, wat betrekking heeft op koolzuur, de geschiedenis ervan, het voorkomen in de natuur en de physische en chemische eigenschappen. Speciale hoofdstukken zijn gewijd aan de commercieële bereiding, zoowel van vloeibaar als van vast koolzuur, en het gebruik ervan.

Inderdaad, een schat van gegevens is in dit werk tezamen gebracht; zoowel de wetenschappelijke werker als de technicus zal het met vrucht kunnen gebruiken; m.i. mag het dan ook in geen bibliotheek van eenige beteekenis ontbreken. Men treft in dit boek tevens vele literatuurgegevens aan, die de waarde aanmerkelijk verhoogen. Een lijst, welke de octrooien opsomt, betrekking hebbend op de fabricage en het gebruik van vast koolzuur, is achterin opgenomen.

Het uitwasschen van koolzuur uit gassen, welke dit gas bevatten, is eenigszins stiefmoederlijk behandeld.

De druk en uitvoering zijn, zooals we in deze serie monografiën gewend zijn, uitnemend verzorgd. Het boek is in ieder opzicht de prijs waard.

A. W. van Seters.

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663.6(022)

J. Holluta, Die Chemie und chemische Technologie des Wassers. Ferd. Enke, Stuttgart, 1937, 219 pp., 16 × 25 cm, RM. 14.80 (—25%).

Het is de bedoeling, dat dit boek zich van andere werken, die zich met „water" bezighouden, hierdoor onderscheidt, dat niet een bepaald gedeelte, b.v. onderzoek of zuivering, uitsluitend wordt behandeld of de hoofdschotel vormt, doch alle vraagstukken, die zich op dit gebied voordoen, worden aangesneden.

In zeker opzicht is deze opzet geslaagd; behalve hoofdstukken over de winning en zuivering van drinkwater, de eisen hieraan te stellen, ketelvoedingwater en wateronderzoek, vindt men o.a. ook de inwerking van water op verschillende bouwstoffen en maatregelen tegen corrosie besproken, alsmede de zuivering van afvalwater van alle soorten bedrijven.

Een gevolg hiervan is echter, dat in dit bestek vrijwel alles slechts zeer oppervlakkig wordt behandeld en het boek ook onevenwichtig is geworden. Zo b.v. worden 21 bladzijden gevuld met gegevens over de samenstelling van verschillende watersoorten, terwijl het gehele wateronderzoek in 9 bladzijden wordt afgehandeld. Ook in het hoofdstuk waterzuivering weet de schr. het belangrijke niet in voldoende mate van het minder belangrijke te scheiden. Het best geslaagd zijn de hoofdstukken over corrosie en over ketelvoedingwater.

Wie zich een globaal inzicht wenst te verschaffen op het gebied van drink- en bedrijfswater zal echter in dit boek zijn wensen ten volle bevredigd zien en in het aanhangsel verwijzingen vinden naar literatuur, die dieper op de afzonderlijke vraagstukken ingaat.

L. H. Louwe Kooijmans.

* * *

546.3 : 669.539.15(022)

A. H. Wilson, The Theory of Metals, University Press, Cambridge, 1936, 272 pp., 14 × 22 cm, geb. 18/—.

Dit boek geeft een fraai overzicht over de metaaltheorie, zoals deze zich, hoewel op het ogenblik nog lang niet afgesloten, toch tot een voorlopig geconsolideerde vorm heeft ontwikkeld. Als inleiding gaat vooraf een hoofdstuk over de klassieke theorie van Lorentz. Vervolgens worden behandeld de algemene theorie van de beweging van electronen in een ideaal rooster en toepassingen op het gebied van legeringstructuur, cohaesie en diamagnetisme. In een ander hoofdstuk komen de optische verschijnselen ter sprake en vervolgens in twee volgende hoofdstukken de theorie der metallische geleiding. Het laatste hoofdstuk is gewijd aan de suprageleiding. In een appendix worden resp. de Fermi-Dirac-statistiek en de oppervlakteverschijnselen behandeld.

De metaaltheorie is ook voor den chemicus van belang, niet in het minst wegens de mogelijkheid, welke voor het eerst de moderne theorie heeft gegeven, om de samenstelling van de intermetallische verbindingen enigszins te begrijpen; verder ook meer in het algemeen in verband met het grote technische belang der metalen.

Dit helder en prettig geschreven boek kan hem daarbij een gids zijn, zo hij met de golfmechanica vertrouwd is. De opzet is geheel theoretisch, experimentele gegevens treft men slechts aan, waar deze ter toetsing van de uitkomsten der theorie worden gebezigd. Dit treedt in Wilson's boek nog meer naar voren dan in het ongeveer gelijktijdig verschenen boek van Mott en Jones en in het bijzonder dan in dat van Fröhlich over dit onderwerp. Voor den chemicus zal dit in het algemeen geen voordeel vormen.

Een bijzonder uitvoerig register verhoogt de gebruikswaarde aanzienlijk.

J. A. A. Ketelaar.

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614.8(022)

Naleving der Veiligheidswet en Ongevallen. Overdruk uit het Centraal Verslag der Arbeidsinspectie over 1936. Algemeene Landsdrukkerij, Den Haag, 1937, 168 pp., 17 × 24 cm, *f* 0.50.

In dit boekje worden systematisch een aantal ongevallen behandeld, die zich in den loop van het verslagjaar 1936 hebben voorgedaan.

Die bedrijfsleiders en hoofden van bedrijven, die, behalve de rentabiliteit en efficiency hunner fabrieken, het lichamelijk welzijn van de arbeiders tijdens het productieproces ter harte gaat, ook zonder dat hun hiertoe van de zijde der Arbeidsinspectie de eisch wordt gesteld, wordt dit boekje vooral ter lezing aanbevolen.

Het blijkt namelijk, dat in vele gevallen ongelukken in fabrieken en werkplaatsen gebeuren, die eerder het gevolg zijn van minder doeltreffende, dan van onvoldoende beveiligingen.

H. P. den Otter.

* * *

621.329.123(022)

Draagbare electrische lampen voor werkzaamheden in ruimten met ontploffingsgevaar. Overdruk uit het Centraal Verslag der Arbeidsinspectie over 1936. Algemeene Landsdrukkerij, Den Haag, 1937, 9 pp., 17 × 24 cm, *f* 0,25.

In dit overdrukje wordt, in eenige bladzijden, mede aan de hand van enkele illustraties, op duidelijke wijze een overzicht gegeven van de beveiligingen, die kunnen worden aangebracht en ook behooren te worden aangebracht aan het electrisch verlichtingsmateriaal, dat gebruikt wordt bij het betreden van ruimten, waarin ontploffingsgevaar bestaat, zooals scheepstanken, enz.

H. P. den Otter.

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666(058)

Agenda pour verrerie, céramique, émaillerie, cimenterie, 1937. Editions Céremver, Bruxelles, 386 pp.

Deze agenda verschijnt in maandelijksche afleveringen. Deze nummers kunnen gesplitst en in een klemband rubrieksgewijs samengevat worden. Feilloos kan dit niet werken, zoolang de uitgever er niet op let, dat niet op één blaadje deelen van twee rubrieken worden afgedrukt. Een voordeel is echter, dat de gebruiker zelf een selectie kan maken.

In het opgenomen onvolledige literatuuroverzicht worden van de meeste artikelen slechts schrijver, titel en plaats genoemd, van enkele is een kort uittreksel aanwezig.

De eveneens onvolledige adreslijsten bevatten de adressen van leveranciers van grondstoffen en machines, van glasfabrieken in België en Engeland. Van de tabellen mogen worden genoemd: chem. samenstelling en smeltpunt van mineralen; berekening van s.g. en uitzettingscoëfficient van glas uit de samenstelling; kwalitatieve chemische analyse; recepten. (Op blz. 317 en 322 staat dezelfde tabel afgedrukt; ook komen vele drukfouten voor).

In de Fransch sprekende landen kunnen zij, voor wie de literatuur in de Duitsche en Engelsche taal niet toegankelijk is, er zeker profijt van hebben.

J. H. D. Heine.

CHEMISCHE KRINGEN.

Groningsche Chemische Kring. In de vergadering van 27 Jan. l.l. hield de voorzitter, Dr. P. A. Okken, een voordracht over *„Nomografie"*. Na een korte inleiding werd de oplossing van de sleutelvergelijking: $f_1(a_1) + f_2(a_2)) = f_3(a_3)$, door middel van het hexogonaal nomogram van d'Ocagne, behandeld. Aangestipt werd hoe, door gebruik te maken van transparanten, met dit nomogram ook de vergelijking:

$$f_1 + f_2 + f_3 + f_4 + \ldots\ldots f_n = 0$$

kan worden opgelost en tevens wat in dit verband kan worden bereikt met binaire schalen. Na terloops de oplossing van de sleutelvergelijking: $1/f_3 = 1/f_1 + 1/f_1$ aangegeven te hebben, wees spr. er op, hoe de oplossing van de sleutelvergelijking $f_2/f_1 = f_3$ ook zonder logarithmen kan geschieden, als men zich eerst met projectieve schalen heeft vertrouwd gemaakt.

Vervolgens werd het bekende ‚drieleidersysteem" besproken en aangegeven, hoe men door invoering van een kromme door middel van het hexogonaal nomogram van d''Ocagne, gemakkelijk tot de oplossing van de sleutelvergelijking:

$$g_1(a_1)f_1(a_3) + g_2(a_1)f_2(a_3) + f_3(a_3) = 0$$

kan geraken. Een belangrijke uitbreiding kan verkregen worden door ook hierbij binaire schalen in te voeren.

De voordracht werd door bespreking van eenige nomogrammen uit de practijk toegelicht.

* * *

Haagsche Chemische Kring. In de vergadering van Dinsdag 18 Januari j.l. heeft Dr. W. Ploeg gesproken over: *„De betrekkingen van Constantijn Huygens tot de natuurwetenschap"*. Op een enthousiaste wijze heeft de spreker deze belangwekkende figuur uit de Gouden Eeuw en de rol, die deze op het gebied der natuurwetenschappen heeft vervuld, besproken.

Constantijn Huygens, die zichzelf in de eerste plaats staatsman achtte, maar bij het nageslacht vooral als dichter bekend staat, is geen natuuronderzoeker geweest, maar hij heeft grooten invloed gehad op de verbreiding van vele belangrijke ontdekkingen uit zijn tijd. Met een tweetal voorbeelden lichtte de spreker dit toe: in de eerste plaats de ontwikkeling van de optica, op welk gebied de uitvinding van den z.g. Hollandschen kijker een omwenteling beteekende, en Huygens' stuwkracht van groot belang is geweest voor het tot stand komen van de publicaties van Descartes, waarin een nieuwe grondslag voor de natuurwetenschap ontwikkeld werd; in de tweede plaats het vraagstuk van de plaatsbepaling op zee, dat de grootste geesten in de 17e eeuw bezighield en waarin Constantijn Huygens een belangrijke rol speelde, in het bijzonder ook bij het tot stand komen van de uitvinding van het slingeruurwerk door zijn zoon Christiaan.

Na de pauze behandelde de spreker de belangstelling van Constantijn Huygens in de chemie. Huygens behoorde tot de weinige verlichte geesten van de 17e eeuw, die de dwaasheid van de alchemie inzagen. Een groote verzameling recepten, door hem bijeengegaard, is bewaard gebleven. Zij betreffen o.a. reukwaters, geneesmiddelen, het waterdicht maken van weefsels, het verhinderen van het roesten van wapens, enz. Veel van wat Huygens op scheikundig gebied blijkbaar moet hebben geweten, is echter verloren geraakt.

In het huishoudelijk gedeelte van de vergadering bracht de secretaris het jaarverslag uit, dat ongewijzigd werd goedgekeurd. Verder werd het financieele beleid van den penningmeester in het afgeloopen jaar goedgekeurd en de contributie voor 1938 op *f* 2.— vastgesteld.

Van het bestuur trad Ir. A. H. Kerstjens af; in zijn plaats werd tot penningmeester benoemd Dr. J. N. Elgersma.

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Leidsche Chemische Kring. Op Donderdag 10 Februari 1938, des avonds te acht uur in het Organisch Chemisch Laboratorium, Hugo de Grootstraat 25, zal Prof. Dr. Jan Smit (Wageningen) spreken over *Bacteriën in huishouding en techniek.*

* * *

Utrechtsche Chemische Kring. Ir. N. Verkinderen van de Gevaertfabriek (Oudegod bij Antwerpen) zal Donderdag 10 Februari spreken over *„Kleurenfotografie".* Deze vergadering vindt plaats in de kleine collegezaal van het Pharmaceutisch Laboratorium, Catharijnesingel 60, aanvang 19.45 uur.

PERSONALIA, ENZ. *)

Aan de Technische Hoogeschool te Delft is bevorderd tot doctor in de technische wetenschap, op proefschrift „Wisselwerking tusschen boorzuur en pentolen", de heer J. M. Furnée, apotheker, geboren te 's-Gravenhage.

* * *

Aan de Universiteit te Leiden is geslaagd voor het candidaatsexamen wis- en natuurkunde F de heer J. Weyl.

* * *

Aan de Technische Hoogeschool te Delft zijn geslaagd voor het examen voor scheikundig ingenieur: Mej. M. J. Smit en de heeren K. E. C. Buyn, G. H. W. Douwes Dekker, D. van Buuren, Dr. F. J. W. Engelhard (met lof), C. W. J. van der Meulen, B. Pennekamp, J. A. Roessingh van Iterson, J. B. Roos, G. E. Rumscheidt en O. B. Schrieke (met lof).

* * *

Binnenkort zal bij G. Naeff te 's-Gravenhage van de hand van Prof. Dr. F. A. H. Schreinemakers een boek over osmose verschijnen, getiteld: Lectures on Osmosis.

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Mejuffrouw Ir. C. S. van Gemerden zal van 15 Februari 1938 a werkzaam zijn bij de N.V. Meelfabriek „de Sleutels" te Leiden

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Dr. W. H. van Mels, rector van het Lorentz-lyceum te Eindhoven, heeft 24 Januari, op uitnoodiging van de Vereeniging voor paedagogisch onderwijs aan de Rijks-Universiteit te Groningen, gesproken over: „Het lyceum, een school in wording". De boeiende rede werd door een levendige gedachtenwisseling gevolgd.

* * *

Natuurkundig Genootschap te Groningen. Dr. W. G. Burgers (Eindhoven) heeft op Dinsdag 25 Januari een zeer interessante lezing gehouden over metaalkristallen, toegelicht door talrijke vernuftige en uitnemend geslaagde proeven. Onder meer projecteerde hij voor het groote auditorium met een electronenmicroscoop de kristallijne structuur van een gloeienden aluminiumdraad en ten slotte toonde de spreker een film van rekristallisatieverschijnselen, opgenomen met een electronenmicroscoop.

TER BESPREKING ONTVANGEN BOEKEN
(aanvragen te richten tot de redactie).

J. A. Kok, Naar het absolute nulpunt. Uitgeverij 't Spectrum. Utrecht, 1937, 96 pp., f 0.90, 11 × 19 cm.

W. Brecht und H. Pfretzscher, Untersuchungen über die Beschwerung der Papiere. Otto Elsner, Berlin, 1947, 119 pp., 15 × 21 cm, RM. 6.

M. Minnaert, De natuurkunde van 't vrije veld, W. J. Thieme & Cie, Zutphen, 1937, 350 pp., 160 fig., 15 × 22 cm, f 3.90, geb f 4.90.

Zeitschrift für angewandte Mineralogie, Gebr. Borntraeger, Berlin, 1937, Recensie-nummer van 19 Januari 1938, 96 pp., 17 × 25 cm.

R. Pönninger, Der künstlich belüftete Tropfkörper, R. Oldenbourg, München, 25 pp., 20 fig., 22 × 31 cm, RM. 5.60.

W. Modest, Das Recht der Öl- und Fettwirtschaft, P. Parey, Berlin, 1938, 262 pp., 15 × 22 cm, RM. 9.60.

Eckstein, Bruno, Turrentine, Kennzeichen des Kalimangels, Verlagsgesellschaft für Ackerbau m.b.H., Berlin, 1937, 235 pp., 41 fig. 55 Tafeln in Vierfarbendruck, 19 × 24 cm, RM. 6.—.

A. C. Morrison. Man in a chemical world Scribner's Sons, Ltd., London, 1937, 292 pp., 10 fig., 16 × 23 cm, $ 3.—.

A. O. Bentley, Text book of pharmaceutics. Tindall & Cox, London, 4e druk, 1937, 1002 pp., 256 fig., 14 × 22 cm, 15/—.

G. de Clercq, Brandstoffenjaarboek 1938. Stooktechnisch adviesbureau, Amsterdam, 211 pp., 11 × 17 cm *f* 0.60.

O. de Vries en C. W. M. Hetterschij, Fosfaathuishouding in een ijzerhoudenden zandgrond, Algemeene Landsdrukkerij, 's-Gravenhage, 1937, 33 pp, 17 × 24 cm, *f* 0.35.

Statistical compilations on aluminium, lead, copper, nickel, quicksilver, silver, spelter and tin, 38th annual issue 1927—1936, Metallgesellsch. A.G., Frankfort am Main, 1937, 117 pp., 21 × 29 cm.

CORRESPONDENTIE, ENZ:

Nieuwe boeken. Hoewel de Redactie geregeld uit tijdschriften en bibliographieën de titels van nieuwe boeken verzamelt en ter recensie aanvraagt (indien de uitgevers hen niet uit eigen beweging inzenden), kan toch menig belangrijk boek aan haar aandacht ontsnappen. Medewerking van belangstellenden, door opgaaf van titels van nieuwe boeken, onder vermelding van de uitgevers, zal zeer op prijs worden gesteld.

* * *

Overdrukjes. Het aantal der gewenschte overdrukjes geve men aan *op het handschrift* boven den titel der verhandeling. Men ontvangt 25 overdrukjes gratis.

Prijsopgaaf van een grooter aantal, een bedrukt omslag, een ander formaat en ander papier wordt op verzoek gezonden.

* * *

Congressen en vergaderingen. Het zal zeer gewaardeerd worden, indien van congressen en vergaderingen, welke voor chemici van belang kunnen zijn, vooraf een mededeeling met programma of agenda aan het Redactiebureau wordt gezonden. Ook verslagen zijn welkom.

* * *

Advertenties. Menige advertentie, die behoorde voor te komen in het Chem. Weekblad, treft men wel elders aan. Men wordt, in het belang van de Nederl. Chem. Vereeniging en haar leden, dringend verzocht, zulke advertenties uit te knippen en in te zenden.

* * *

Afkortingen van tijdschriftnamen. Men gebruike de afkortingen vermeld in Chem. Jaarboekje II op blz. 12—14. Indien men andere gebruikt, moeten zij op het Redactiebureau veranderd worden, hetgeen vertraging veroorzaakt.

* * *

Men wende zich tot het *Redactiebureau* (Zoeterwoudsche Singel 18, Leiden) **uitsluitend schriftelijk.**

De *hoofdredacteur* is telefonisch (No. 1449) het beste te bereiken des morgens tusschen 8 u. en 8 ³/₄ u. en 's namiddags tusschen 5 u. 30 en 7 u. 30.

Aangeboden betrekkingen.

Voor een fabriekslaboratorium wordt gevraagd een jonge chem. ingenieur of acad. gevormde chemicus. Zie verder de adv. in No. 4.

* * *

Op een laboratorium in het Noorden des lands kan onmiddellijk geplaatst worden een scheikundige. Zie verder de adv. in No. 5.

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*) Berichten voor deze rubriek zijn steeds welkom.

Nederlandsch-Amerikaansche fundatie. Zie blz. 94.

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Gevraagd een jonge, manlijke of vrouwelijke chemicus voor literair organisch-chemisch werk. Zie verder de adv. in No. 5.

Gevraagde betrekkingen *).

No. 271. Scheik. ing., dr. in de scheikunde, Nederlander, 40-iger, langdurige veelzijdige binnen- en buitenlandsche ervaring in leidende functies bij wereldconcern, wil van positie veranderen (hier te lande of buitenland). Goede talenkennis, bereisd, vlugge inwerking. Zeer goede referenties.

No. 411. Scheik. ing., diploma Delft 1936, 1 jaar praktijk, zoekt verandering van betrekking.

No. 491. Apotheker-scheikundige, 30 jaar, met ervaring van een veelzijdig handelslaboratorium, goed bekend met de voedingsmiddelenchemie en practijk in het onderzoek van giftige gassen, zoekt betrekking.

No. 504. Chem. docts., 25 jaar, physico-chem. (colloidchemie), ook org. en bact. goed onderlegd, zoekt werkkring, evt. commerciëel en (of) buitenland. Kan zelfstandig werken; eenige ervaring in doceeren; kennis van octrooizaken, moderne talen; vrij van militairen dienst, ook in Ned.-Indië, goede gezondheid, Uitstekende referenties.

No. 515. Chem. docts., bacterioloog en pharmacoloog, bekend met pharmaceutische industrie, zoekt verandering van betrekking.

No. 519. Dr. in de scheik., bacterioloog, 6 jaar researchervaring in zuivelbacteriologie en -chemie, zoekt verandering van werkkring.

No. 520. Chem. drs., m., 23 jaar, physico-chemicus met eenige analytische en organ. preparatieve ervaring en goede talenkennis (ook Russisch) zoekt betrekking, eventueel ook buitenland.

VRAAG EN AANBOD.

Correspondentie wordt over deze rubriek niet gevoerd: de Redactie zendt alleen brieven door, *waarvoor men porto insluite.*

Ter overneming gevraagd:

Chem. Courant 1930 t/m 1936.

Ter overneming aangeboden:

Chem. Weekblad 1920 t/m. 1937 in losse afl.
Rec. trav. chim. 1920 t/m. 1923.
Abegg, Handb. anorg. Chemie, 7 dln, geb.
Samec, Kolloidchemie d. Stärke (1927).
Dienemann-Burre, Die nutzbaren Gesteine Deutschlands (1929).
v. Royen-de Vooys, Mech. Techn., II, 3e stuk, 1e ged., Papierfabr. (1917).
Microscoop-optiek, O. Seibert, Wetzlar.
R. B. Hough, American woods, part 1, 1910.
J. W. Mellor, Modern inorg. chem., 1927.
I. P. de Vooys, Aardewerk- en glasfabricage, malerijen, 1926.
I. P. de Vooys, Papierfabricage, drukkerij, 1921.
I. P. de Vooys, Textielnijverheid, 1925.
Matthews, Textile fibers, 1924.
L. E. Weber, The chemistry of rubbermanufacture, 1926.
R. Zsigmondy, Kolloidchemie I, Algem. Teil, 1925.
L. Gattermann, 1930.
Doos met gewichten van 2 mg—50 g.

De opgaaf van het aangebodene en gevraagde wordt driemaal geplaatst. Wenscht men daarna nog plaatsing, dan is daarvoor een nieuwe opgaaf noodig. Men wordt dringend verzocht, dadelijk kennis te geven, indien plaatsing niet meer noodig is.

Economische Berichten.

Nadere inlichtingen verstrekt het Bureau van de Vereeniging van de Nederlandsche Chemische Industrie, Laan Copes van Cattenburch 16, te Den Haag [1]).

Griekenland.

*Wijziging invoerrechten.** Ingaande 15 Januari j.l. zijn de omrekeningscoëfficiënten van goud- in papierdrachmen, voor onderstaande producten als volgt gewijzigd (tusschen haakjes de oude coëfficiënten):

Tarief no. 16 oliehoudende vruchten en zaden 36 (15); tarief no. 159 g. 9 chromaten 30 (20).

*Tariefwijzigingen.** In het Douanetarief zijn de volgende wijzigingen aangebracht:

Tarief no. 18c. 3 paraffine max. 50 (140) gouddr. per 100 kg, min. 32 (115) gouddr. per 100 kg.

Tarief no. 18c. 4 ceresine en alle andere niet afzonderlijk vermelde wasproducten max. 140 (140) gouddr. per 100 kg; min. 115 (115) gouddr. per 100 kg.

Bovenstaande rechten dienen te worden verhoogd met 75 opcenten. De oude rechten zijn tusschen haakjes aangegeven.

Oostenrijk.

*Betaling van vrachtkosten.** Blijkens mededeeling van Harer Majesteits Gezant te Weenen heeft de Oostenrijksche Nationale Bank bepaald, dat het verstrekken van een vergunning om deel te nemen aan de zgn. particuliere clearing met ingang van 1 Februari a.s. afhankelijk wordt gesteld van de voorwaarde, dat de vrachten voor het spoorwegvervoer van Europeesche zeehavens tot aan het Oostenrijksche station van aankomst, respectievelijk het grensstation, van te voren in Oostenrijk bepaald zijn. Is aan die voorwaarde niet voldaan, dan worden geen deviezen toegestaan voor den invoer.

Deze maatregel is genomen, teneinde het voor Oostenrijk in Duitschland uitstaande clearingssaldo te verminderen, doordat de transportkosten, wegens doorvoer door Duitschland verschuldigd, ten laste van dit saldo zullen worden vereffend.

Uruguay.

*Betalingsverkeer.** In aansluiting op het bericht in het Chemisch Weekblad van 1 Januari j.l. op pag. 20, kan nu bericht worden, dat de Regeering van Uruguay op 10 dezer, eenige decreten met betrekking tot de beschikbaarstelling van deviezen heeft uitgevaardigd.

1. Bij beschikking van 18 December, No. 1787/937, is bepaald, dat vanaf de eerste maand, waarin goederen geland zijn, welker consignatarissen steeds de deviezenvoorschriften van de Bank der Republiek zijn nagekomen, dezen voor een duur van 90 dagen vrijgesteld zijn van de betaling van het z.g. „derecho de piso" (opslagrecht). Volgens de considerans van het decreet wordt hiermede hoofdzakelijk beoogd den gang van zaken voor de ontvangers van bouwmaterialen te vergemakkelijken, teneinde te voorkomen, dat reeds aangevangen werken zullen moeten worden stopgezet. Rechthebbenden op de in de douane opgeslagen koopwaren zullen van deze bepalingen kunnen profiteeren.

2. Het tweede decreet slaat op den invoer van koopwaren op consignatiebasis door firma's, die geregeld zaken op deze wijze doen. Twee keeren jaarlijks, vanaf 1 Januari j.l., zal de Bank der Republiek een globaal contingent opgeven voor de *consignatie-invoeren* afkomstig van de landen, welke over een deviezencontingent beschikken. De Honoraire Commissie voor Invoer en Deviezen zal in overeenstemming met de Bank der Republiek binnen vorenbedoeld contingent aan elk der firma's, geïnteresseerd in consignatiezaken, een individueel contingent toewijzen, in aanmerking nemende, de soort en de herkomst der waren, de in vroegere perioden afgesloten zaken, enz.

3. Het derde decreet, eveneens van 18 December, is voor de Nederlandsche exportindustrie vermoedelijk van meer belang. Het bepaalt, dat de importeurs, alvorens hunne aankoopen in het buitenland definitief af te sluiten, zich van een „permiso previo" moeten verzekeren, dat door de Honoraire Commissie voor Invoer en Deviezen zal worden afgegeven. Deze voorafgaande vergunning zal binnen 48 uur na ontvangst van de betrokken aanvrage worden verleend, behoudens zeer bijzondere omstandigheden. Anderzijds zal evengenoemde Commissie de voorwaarden kunnen aangeven, onder welke het den importeurs geoorloofd zal zijn desgewenscht van de reeds verleende vergunningen geen gebruik te maken. De termijnen, binnen welken de goederen in Uruguayaansche havens moeten aankomen, overeenkomstig decreet van 6 April 1935 is verlengd tot 180 dagen, te rekenen vanaf den datum der aanvrage van de invoervergunning. Bepaald is voorts, dat de Commissie hiervorengenoemd, dagelijks een staat van disponibele deviezen zal opmaken, welke minstens eenmaal per week aan de Bank der Republiek zal worden opgegeven. Bovendien zal de Commissie onmiddellijk de Bank der Republiek verwittigen, indien de diverse contingenten tot een bedrag van 80 % zullen zijn opgenomen.

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*) Plaatsing gratis voor leden.
Brieven te richten tot de Chem. Arbeidsbeurs, 's-Gravenhage, Willem Witsenplein 6 (*met ingesloten porto voor doorzending*).
Men wordt verzocht dadelijk bericht te zenden, indien de plaatsing niet meer noodig is.

[1]) De met * gemerkte berichten zijn ontleend aan gegevens, verstrekt door den Economischen Voorlichtingsdienst van het Departement van Economische Zaken.