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Normal Vorticity Jump Condition Across a Magnetogasdynamic Discontinuity

HAYES[1] showed that the normal jump in the vorticity across a gas-dynamic discontinuity is zero. In this note it is shown that the same conclusion is no more true across a magnetogasdynamic discontinuity.

The fundamental system of equations of discontinuties in magneto-fluid-dynamics is[2]

$$\varrho\, q_n \left[w + \frac{1}{2} q_n^2 + \frac{1}{2} \bar{q}_t^2 + \bar{H}_t^2/4\pi\varrho \right] = H_n [\bar{H}_t \cdot \bar{q}_t]/4\pi , \tag{1}$$

$$[p] + \varrho\, q_n [q_n] + [\bar{H}_t^2]/\vartheta\pi = 0 , \tag{2}$$

$$\varrho\, q_n [\bar{q}_t] = H_n [\bar{H}_t]/4\pi , \tag{3}$$

$$H_n [\bar{q}_t] = [q_n \bar{H}_t] , \tag{4}$$

where the suffix n denotes the component of a vector along the unit normal vector $\bar{n}$ to the discontinuity surface and suffix t denotes two-dimensional tangential component. The square bracket denotes the jump in the quantity enclosed. Let us define the density-strength of the discontinuity by $\delta = [\varrho]/\varrho_1$, where suffix 1 denotes the value of the quantity just ahead of the discontinuity. Then, using (3) and (4) and the relations $[\varrho\, q_n] = 0$ and $[H_n] = 0$, we get

$$[\bar{q}_t] = \frac{\delta H_{1n}\, q_{1n}}{4\pi\varrho_1 q_{1n}^2 - (1+\delta) H_{1n}^2} \bar{H}_{1t} . \tag{5}$$

The density-strength δ is expressible in terms of the flow variables just ahead of the discontinuity by using the relations (1), (2), (3) and (4)[3]. The vorticity $\bar{\zeta}$ is defined as curl $\bar{q}$ and can be expressed as

$$\bar{\zeta} = \bar{n} \times (\bar{n} \cdot \nabla)\, \bar{q} + \nabla_t \times \bar{q} , \tag{6}$$

where the subscript t on the nabla operator indicates that only the tangential part of the derivative is included. The operators $[\ ]$ and ∇_t are commutable and therefore, taking a jump in (6) across a discontinuity we have

$$[\bar{\zeta}] = \bar{n} \times [(\bar{n} \cdot \nabla)\, \bar{q}] + \nabla_t \times [\bar{q}] . \tag{7}$$

Also, since $\bar{n}$ is the gradient of the normal coordinate n, we see that $\nabla_t \times \bar{n} = 0$. Now taking dot product of (7) with $\bar{n}$, we have

$$[\zeta_n] = \bar{n} \cdot (\nabla_t \times [\bar{q}_t]) . \tag{8}$$

Substituting from (5) in (8) it can easily be seen that the normal jump in the vorticity is not zero. If we assume that the flow ahead of the discontinuity is uniform, the right hand side of (8) can be expressed in terms of the curvature tensor k of the discontinuity surface and the flow and field parameters just ahead of the discontinuity by using $\nabla\bar{n} = -k$ and the jump conditions[3].

Résumé. HAYES[1] a démontré que le saut normal dans la vorticité, à travers une discontinuité dynamique-gaz, est égale à zéro. On a trouvé que cette conclusion n'est plus vraie dans le cas d'une discontinuité magneto-gaz-dynamique.

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[1] W. D. HAYES, J. Fluid Mech. *2*, 595 (1957).

[2] L. D. LANDAU and E. M. LIFSHITZ, *Electrodynamics of Continuous Media* (Pergamon Press, New York 1960).

[3] R. P. KANWAL, J. Math. Mech. *9*, 681 (1960).

Magnetitfördernde Wirkung von Al^{3+}-Ionen bei der Luftoxidation des $Fe(OH)_2$

Wenn man das $Fe(OH)_2$ bei Raumtemperatur im sauren Medium ($FeSO_4$:NaOH = 1:1) fällt und oxidiert, so bildet sich γ-FeOOH[1]. Bei annähernd stöchiometrischer Füllung tritt Magnetit neben α-FeOOH auf, während im alkalischen Milieu ($FeSO_4$:NaOH = 1:3) ausschliesslich α-FeOOH aufkommt[2]. Das hängt mit der Lage der isoelektrischen Punkte des γ-FeOOH (pH $\sim$ 5,4)[1] sowie des $Fe(OH)_2$ (pH $\sim$ 12)[3] zusammen. Wenn Magnetit ($Fe^{II}Fe_2^{III}O_4$) entstehen soll, so muss das γ-FeOOH negativ und das $Fe(OH)_2$ positiv aufgeladen sein. Bei alkalischer Fällung ist der isoelektrische Punkt des $Fe(OH)_2$ bereits überschritten, so dass dieses bei Oxidation völlig in dreiwertiges Eisen übergeht. Doch rufen Al^{3+}-Ionen unter diesen Umständen eine leichte Magnetitbildung hervor, was offenbar so zu erklären ist, dass das Aluminatanion geringe Mengen $Fe(OH)_2$ adsorptiv festhält und

Luftoxidation von $Fe(OH)_2$ im alkalischen Medium bei 20 °C, auch bei Zusatz von Al^{3+}

Nr.	Mol. Verh. $FeSO_4$: NaOH	Atom-verh. $Fe^{2+}:Al^{3+}$	Die Oxidationsprodukte								
			Farbe	% Fe_2O_3	% FeO	% Al_2O_3	% SO_3	% H_2O	Ferromagnetismus direkt	bei 300°	Röntgenbefund
1	1:3	1:0	gelbbraun	83,5	0,0	–	0,05	16,4	0	0	α-FeOOH
2	1:3	1:0,02	braun	82,4	0,2	0,8	0,03	16,6	schwach		α-FeOOH + einige schwache Magnetitlinien
3	1:3	1:0,2	dunkel-braun	75,7	1,9	7,5	0,03	14,9	deut-lich	deut-lich	α-FeOOH + Magnetit

eine Zeitlang vor der Oxidation schützt, bis dieses zur Bildung des Magnetits verbraucht wird, das übrigens kaum luftempfindlich ist. Die betreffenden Präparate waren daher FeO-haltig, ferromagnetisch und zeigten das Magnetitgitter. Bei saurer und stöchiometrischer Fällung des $Fe(OH)_2$ hatte das Al^{3+} keinen Einfluss auf die Qualität der Oxidationsprodukte.

Zwecks Ausführung der Versuche löst man 6 g $FeSO_4 \cdot 7H_2O$ in 100 cm^3 destilliertem Wasser und versetzt dieses bei 20 °C mit 1 *N* NaOH in einem Mol.-Verhältnis $FeSO_4$:NaOH = 1:3. Al^{3+}-Ionen verwendet man in Form von $Al(NO_3)_3 \cdot 9H_2O$ in einem bestimmten Atomverhältnis $Fe^{2+}:Al^{3+}$. Nach Auffüllung mit destilliertem Wasser auf 200 cm^3 behandelt man das Reaktionsgemisch 3 Std. mit einem Luftstrom (1,6 l/min) bei 20 °C. Die sorgfältig ausgewaschenen und luftgetrockneten Oxidationsprodukte wurden auf ihre Zusammensetzung geprüft, worüber die Tabelle Auskunft gibt.

Summary. It has been proved that $Fe(OH)_2$, precipitated in alkaline solution and oxidated by air-oxygen, transforms to α-FeOOH. In presence of Al^{3+}, besides α-FeOOH magnetite also appears.

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1 A. KRAUSE, Z. anorg. allg. Chem. *174*, 145 (1928).
2 A. KRAUSE und A. BORKOWSKA, Z. anorg. allg. Chem. *326*, 216 (1963).
3 A. KRAUSE und A. BORKOWSKA, Roczn. Chem. *29*, 999 (1955).

Structure and Activity of Corticotrophic Peptides: Synthesis and Biological Activity of Two Corticotrophic Peptides with Neutral Amino Acids in Positions 17 and 18

Positions 17 and 18 in the amino acid sequence[1] of ACTH are of considerable importance, since appreciable stimulation of the adrenal cortex only occurs if the chain length exceeds 16 amino acids, starting from the amino end of the molecule[2–5]. In the natural sequence these positions are occupied by two arginine residues, which are known to be strongly basic (Table I). If these are replaced, in synthetic ACTH fragments, by the less basic ornithine or lysine residues, corticotrophic activity is retained[6,7]. It is even intensified if serine in position 1 is in the D-form instead of the L-form[8–13].

In order to assess the influence of a further decrease in basicity in positions 17 and 18 with regard to biological activity, we synthesized the two nonadecapeptides Xa and Xb. They are substituted in both positions 17 and 18 by the neutral amino acids norvaline (Xa) and norleucine (Xb) and have D-serine in position 1.

Norvaline has the same alkyl side chain as arginine and ornithine, and norleucine the same alkyl side chain as lysine, both being devoid of the respective basic groups. Moreover, the length of the norleucine side chain is equal to that of the ornithine side chain (including the basic group).

Synthesis. The synthesis was carried out in the same way for both the a and b series of the compounds (numbers refer to formulae in Table II): I was reacted with hydrazine hydrate to produce the hydrazide II, which was condensed with proline amide to III by the method of HONZL and RUDINGER[14]. Catalytic hydrogenation of the benzyloxycarbonyl group led to compound IV, which was coupled with Z-Lys(Boc)-Pro-Val-Gly-Lys(Boc)-Lys(Boc)-N_3 (prepared in situ from the corresponding hydrazide V[10] by HONZL and RUDINGER's method[14]), forming the protected, crystalline nonapeptide amides VI. Removal of the benzyloxycarbonyl group, again by catalytic hydrogenation, gave VII, and condensation with Boc-D-Ser-Tyr-Ser-Met-Glu(OBut)-His-Phe-Arg-Trp-Gly-OH VIII[12] by the carbodiimide method yielded IX. These fully protected nonadecapeptide amides IXa and IXb were purified by countercurrent-distribution. Then all protecting groups were split off with trifluoroacetic acid. Finally, the resultant trifluoroacetates were

Table I. β-Corticotrophin-(1-24)-tetracosipeptide (Synacthen®)[16]

H-Ser	Tyr	Ser	Met	Glu	His	Phe	Arg	Trp	Gly	Lys	Pro	Val	Gly	Lys	Lys	Arg	Arg	Pro	Val	Lys	Val	Tyr	Pro-OH
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24