

normale Stellung zueinander haben, das heisst, wenn beim Kieferschluss die oberen Nagezähne die unteren übergreifen (Abb. 3, links). Mit den oberen Zähnen wird die Nahrung, eine Rübe zum Beispiel, festgehalten, in der Hauptsache mit den unteren wird das Nagen besorgt. Bleibt nun der Oberkiefer im Wachstum zurück, so greifen die Nagezähne schliesslich nicht mehr übereinander, sondern stossen aufeinander. Dies beeinträchtigt bereits die Funktion der Zähne, sie nutzen sich nicht mehr keilförmig ab, sondern flach (Abb. 3, Mitte). Bei noch stärkerer Verkürzung des Oberkiefers kommen die Nagezähne in umgekehrte Stellung als normal, die unteren Inzisiven greifen jetzt beim Kieferschluss über die oberen. Damit sind die Zähne ausser Funktion gesetzt, vermögen sich nicht mehr abzunutzen und werden überlang (Abb. 3 rechts). Einem solchen Kaninchen wächst innerhalb verhältnismässig kurzer Zeit das Maul regelrecht zu, es muss verhungern, wenn es nicht künstlich mit Weichfutter ernährt wird und die Nagezähne immer wieder abgekniffen werden. So wirkt sich hier die an sich harmlos erscheinende Kieferanomalie infolge der Besonderheit der Nagezähne letal aus.

Fassen wir zusammen. Das Gengefüge im System voneinander entfernt stehender Arten, wie Mensch

und Kaninchen, ist verschieden. Viele *Einzelgene* haben aber auch diese Säuger gemeinsam. Die Mutabilität homologer Gene bewegt sich in den gleichen Bahnen und führt zu übereinstimmenden Änderungen im Erbbild. Ob im Erscheinungsbild der Individuen übereinstimmende Änderungen erzielt werden, hängt von dem Gengefüge der jeweiligen Arten ab, von ihren art-, gattungs-, familienspezifischen Merkmalen. In jedem Falle aber vermag uns die vergleichende experimentelle Methode durch den Modellversuch am Tier für das Verständnis der menschlichen Erbliden wichtige Erkenntnisse zu vermitteln.

### Summary

The mutation of homologous genes can produce the same changes in phenotype in different mammals, animals as well as human beings. In this way the same hereditary disease can arise in man and animal. This fact permits the study of human hereditary diseases in model experiments in animals under conditions impossible to be realized in man. How far the parallelism between human beings and animals can be taken and where the limits of this parallelism are, which are the problems of the comparative heredo-pathology in detail, and how these problems may be attacked, is demonstrated here in numerous examples.

## Brèves communications - Kurze Mitteilungen Brevi comunicazioni - Brief Reports

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### Energy Content of Propellants and of Explosives

With the advent of jet propulsion some new chemical problems have made their appearance which have certain peculiar characteristics not ordinarily considered. For instance, in order to estimate the value of a self-contained propellant combination incorporating both fuel and oxidizer it is important to know the energies  $q_m$  and  $q_v$  respectively which 1 g or 1 cm<sup>3</sup> of such a propellant can release. It is likewise important to know the volume of gas generated per gram and per cm<sup>3</sup> of total propellant as well as a certain average ratio  $\bar{v}$  of the specific heats  $c_p$  and  $c_v$  at constant pressures and constant volumes respectively of the reaction products through an adequate range of temperatures<sup>1</sup>. All of these problems which are also of importance if one wishes to calculate the power of chemical explosives can be satisfactorily dealt with through a general morphological analysis, which will be reported upon in another place. We here wish to call attention only to a few

factors which decisively influence the values  $q_v$ , that is the energies generated per unit volume of the originally solid and liquid propellants or explosives.

*Propellants and explosives with gaseous reaction products.* We first notice that common explosives and propellants generate at best energies  $q_v$  which are in the range 1-3 kcal/cm<sup>3</sup>. This is in particular true for those reagent complexes which contain no other elements besides carbon, hydrogen, nitrogen and oxygen. In Table I a few of these are listed.  $q_m$  is the energy generated per gram while  $\bar{v}$  is the average density of the explosive. Thus  $q_v = \bar{v} \times q_m$  is the energy released per cm<sup>3</sup> of the original combination.

The reaction products in all of the cases listed are *gaseous*. This fact limits the values of  $q_v$  for two fundamental reasons. First, in order to achieve all gaseous components the original solid explosives may first thought to be sublimated and subsequently reacted. The heats of sublimation are thus essentially lost. Secondly, gases such as H<sub>2</sub>O, CO and CO<sub>2</sub> dissociate relatively easily at the elevated temperatures resulting from an explosion and the values of  $q_v$  are thus further depressed.

<sup>1</sup> F. ZWICKY, J. Amer. Rocket Soc. 34, 3 (1951).

Table I

Propellant	$q_m$ kcal/g	$\bar{\rho}$ g/cm <sup>3</sup>	$q_v$ kcal/cm <sup>3</sup>
C(amorphous) + O <sub>2</sub> (liquid) . . .	2.08	1.28	2.67
C(amorphous) + 2O <sub>3</sub> (liquid) . . .	1.49	1.71	2.60
2H <sub>2</sub> (liquid) + O <sub>2</sub> (liquid) . . . .	3.60	0.42	1.52
C <sub>6</sub> H <sub>5</sub> N <sub>3</sub> O <sub>7</sub> TNT . . . . .	0.63	1.65	1.04
CH <sub>3</sub> NO <sub>2</sub> Nitromethane . . . . .	1.06	1.13	1.20
C <sub>7</sub> H <sub>5</sub> N <sub>5</sub> O <sub>8</sub> Tetryl . . . . .	0.87	1.73	1.51
C <sub>3</sub> H <sub>8</sub> N <sub>6</sub> O <sub>6</sub> RDX . . . . .	1.22	1.82	2.22
C <sub>3</sub> H <sub>5</sub> N <sub>3</sub> O <sub>9</sub> Nitroglycerin . . .	1.51	1.59	2.40
C(CH <sub>2</sub> ONO <sub>2</sub> ) <sub>4</sub> PETN . . . . .	1.40	1.77	2.47

In considering fluorine, chlorine, and other oxidizers similar conditions prevail. One may therefore state generally that if all reaction products of a chemical composition are gaseous the energy  $q_v$  released per cm<sup>3</sup> of the original composition is less than about 3 kcal/cm<sup>3</sup>.

*Reagents which give rise to solid and liquid reaction products.* From the considerations given above it follows that heats of reaction superior to 3 kcal per cm<sup>3</sup> of the original reagent composition can only be expected if the reaction products contain liquid and solid components. In Table II a few examples are listed which bear out this expectation.

Table II

Reagent Composition	$q_m$ kcal/g	g/cm <sup>3</sup>	$q_v$ kcal/cm <sup>3</sup>
Ti + C = TiC . . . . .	1.83	3.66	6.70
Ca + 2Si = CaSi <sub>2</sub> . . . . .	2.3	1.81	4.16
Fe <sub>2</sub> O <sub>3</sub> + 2Al = 2Fe + Al <sub>2</sub> O <sub>3</sub> . . .	0.85	4.75	4.03
8Al + 3KClO <sub>4</sub> = 3KCl + 4Al <sub>2</sub> O <sub>3</sub> . .	2.40	2.58	6.20
3PbO <sub>2</sub> + 4Al = 2Al <sub>2</sub> O <sub>3</sub> + 3Pb . . .	0.68	7.1	4.85
4Al + 3H <sub>2</sub> O <sub>2</sub> = 2Al <sub>2</sub> O <sub>3</sub> + 3H <sub>2</sub> . .	2.50	1.91	4.80

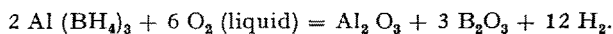
It is thus seen that as soon as for instance carbon in the solid state is retained in the reaction products or appropriate solids such as Al<sub>2</sub>O<sub>3</sub> are formed, the energies released per cm<sup>3</sup> of the original compositions can be materially greater than  $q_v = 3$  kcal/cm<sup>3</sup> which roughly represents the upper limit of what can be achieved with explosives giving rise to gaseous reaction products only.

*Practical applications.* Although it is an advantage in some cases to use propellants for rockets whose energy content per unit volume rather than per gram is as high as possible, it is usually more important that in addition to sufficiently large values of the specific heats  $c_p$  and  $c_v$  per gram and of their ratio, the energy  $q_m$  available per gram be great. On the other hand, explosive power is intimately related to great energy content per unit volume. In addition it is naturally imperative that an explosive also generate at least a moderate amount of gas in order to transfer the energy generated rapidly to the surrounding medium. A composition such as "thermit" shown in the third row of Table II is very ineffective as an explosive in spite of its elevated value of  $q_v$ . This consideration leads to the following two suggestions of how one is to proceed.

The first suggestion is to combine gas generating explosive compositions such as they are shown in Table I

with compositions of the type shown in Table II. Thus one may for instance immerse pellets or granules of thermit in nitromethane, TNT and so on, and explode the mixture with the desired effects.

The second suggestion is to incorporate the desirable elements chemically, rather than physically in the original explosives. As an illustration the following reaction may be considered:



Here the oxidation of aluminum and boron furnishes the desired heat of reaction while the released hydrogen provides for the necessary gas. Since aluminum borohydride has a heat of formation which is roughly equal to zero we obtain 1260 kcal as the total heat released for the above combination in gram moles.

From this it follows that  $q_m = 3.75$  kcal per gram of the original propellants, whose average density is  $\rho = 1.08$  g/cm<sup>3</sup>. Consequently,  $q_v = 4.07$  kcal/cm<sup>3</sup>. The volume of hydrogen generated is about 800 l per kg of the original chemical composition, a volume which is quite adequate when compared with the amounts of gases obtained from conventional explosives. For the compositions of Table I the maximum amounts of gas generated range from 510 l/kg for C + O<sub>2</sub>(liquid) to about 1100 l/kg for nitromethane and 1240 l/kg for the liquids of 2H<sub>2</sub> + O<sub>2</sub>. Instead of liquid-liquid propellants, as in the example, one may of course also use solid-solid compositions such as 2LiBH<sub>4</sub> + KClO<sub>4</sub>. From these considerations it follows that the simple and the combined hydrides and nitrides of such light elements as Li, Be, B, Na, Mg, Al, Si and so on are promising candidates as components for powerful explosive compositions.

Some of the combinations shown in Table II may of course be quite useless as explosives or additives to explosives unless they can be brought themselves to detonate. There are several means to accomplish this, but these will not be discussed here. It may only be mentioned that Al (BH<sub>4</sub>)<sub>3</sub> is "hypergolic" with O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> at room temperature, that is, it reacts on contact with these substances. Actually the corresponding reactions are quite explosive in character and release in fact per cm<sup>3</sup> the high energies which we have quoted in the preceding. Most light element borohydrides as well as aluminohydrides<sup>1</sup> react (hydrolyze) explosively on contact with H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. Aluminum and magnesium powder in watery suspension can be detonated by the application of proper thermomechanical shocks. The same is true for most of the reactions shown in Table II. Whenever any of these reactions go to completion the energies released per cm<sup>3</sup> are of course equal to those calculated from thermochemical principles and thus the simple theorem which has been discussed in this note is confirmed by a great variety of experimental data.

Mixtures such as thermit and others of the types shown in Table II may be used to form solid inserts for sharpened charges upon whose detonation these inserts are ignited and ejected at high speed. Self reacting particles are accelerated to higher velocities and possess in general higher power of penetration than those obtained from the conventional inert solid inserts<sup>2</sup>. Also, projectiles within which a chemical reaction of the type shown in Table II takes place can be used as artificial meteors which in contradistinction to natural meteors

<sup>1</sup> D. T. HURD, *Chemistry of the Hydrides* (John Wiley & Sons, Inc., New York, 1952).

<sup>2</sup> G. BIRKHOFF, D. P. MACDOUGALL, E. M. PUGH, and G. TAYLOR, *J. Appl. Phys.* 19, 563 (1948).

are luminous even when travelling through a very high vacuum such as it exists in interplanetary space<sup>1</sup>.

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California Institute of Technology, Pasadena, California, February 22, 1954.

### Zusammenfassung

Gewöhnliche Explosivmittel und Raketentriebstoffe entwickeln nach Zündung Reaktionswärmen, welche den Wert  $q_v = 3$  kcal je  $\text{cm}^3$  nicht überschreiten. Dies gilt besonders für Kombinationen, die nur Kohlenstoff, Wasserstoff, Stickstoff und Sauerstoff enthalten. Da die Reaktionsprodukte solcher Triebstoffe alle gasförmig sind, geht im wesentlichen die Sublimationswärme der ursprünglich festen Stoffe verloren, und die Werte von  $q_v$  erscheinen entsprechend niedriger. Im gleichen Sinne wirkt die relativ leichte Dissozierbarkeit von  $\text{CO}$ ,  $\text{CO}_2$  und  $\text{H}_2\text{O}$  bei den resultierenden Explosionstemperaturen. Um grössere Werte von  $q_v$  zu erzielen, müssen deshalb Elemente, wie Lithium, Bor, Magnesium, Aluminium und Silizium, in die Explosivstoffe eingebaut werden, die nach Detonation feste und flüssige Oxyde und Verbindungen liefern. Es wird an Hand einiger Beispiele gezeigt, dass auf diese Weise Energiemengen verfügbar werden, die im Bereich von 4 bis 7 kcal je  $\text{cm}^3$  liegen. Zur praktischen Ausführung können die genannten Leichtelemente entweder physikalisch einem gewöhnlichen Explosivstoff beigemischt werden, oder es können diese Elemente mit Wasserstoff, Stickstoff und eventuell Sauerstoff, Fluor usw. zur Verbindung gebracht und mit einem zusätzlichen Oxydationsmittel reagiert werden. Falls man in explosiven Hohlladungen potentiell selbstreagierende Einlagen aus komprimiertem Thermit oder ähnlichen Kompositionen benutzt, werden nach Detonation glühende Teilchen grosser Geschwindigkeit und grosser Durchdringungsfähigkeit ausgeschleudert. Diese Teilchen können auch als in einem Vakuum wie dem interplanetarischen Raum selbstleuchtende künstliche Meteore zu Experimenten verschiedener Art benutzt werden<sup>2</sup>.

<sup>1</sup> F. ZWICKY, Engineering and Science Monthly, Calif. Inst. of Technology, Pasadena, January 1953.

<sup>2</sup> G. BIRKHOFF, D. M. MACDOUGALL, E. M. PUGH and G. TAYLOR, J. Appl. Phys. 19, 563 (1948).

### The Relative Stabilities of *Cis* and *Trans* Isomers

The original rule for determining from physical properties which isomer in a cyclic system was *cis* and which was *trans* was proposed by VON AUWERS<sup>1</sup>. Unfortunately, this rule was found not to hold true in several cases and much confusion has been caused thereby. Most of these cases in which the rule of VON AUWERS fails to predict the isomers correctly show a consistency, a consideration of which has prompted a restatement of the original rule. With respect to *cis* and *trans* isomers in cyclic systems, that isomer which has the highest boiling point, highest index of refraction and highest density is the isomer which possesses the least stable configuration. It is apparent that the structures predicted by this rule will differ from those predicted by VON AUWERS rule only when the *trans* isomer is less stable than the *cis*.

The rule stated above is substantiated by an amount of experimental evidence which is too large to be discussed here except for certain cases of particular importance. It need only be said that of the hydrocarbons listed in various compilations<sup>1</sup>, no exception to the rule was found<sup>2</sup>. Compounds containing functional groups were not exhaustively considered, but out of some dozen cases examined the predictions of the rule were confirmed with only one questionable case<sup>3</sup>.

Three critical cases may be specifically mentioned. *cis*-1, 3-Dimethylcyclohexane is known<sup>4</sup> to be more stable than the *trans* isomer, and it was also recently shown that the same is true of the 1, 3-dimethylcyclopentanes<sup>5</sup>. A somewhat different type of system, [0, 3, 3]-bicyclo-octane, also has a more stable *cis* isomer in contrast with the homologous hydrindanes<sup>6</sup> and decalins. In each of these cases the correct structures are predicted by the rule stated.

Although there is little evidence available<sup>1</sup> to support the contention, it is reasonable to suppose that the rule will apply to more highly substituted systems and likewise to small- and large-ring compounds, and will thus be of practical value since the relative stabilities of the compounds can be determined in most cases by conformational analysis<sup>7</sup>.

The existence of the rule stated above can be rationalized by qualitative theoretical considerations. An ideal case is a pair of simple *cis* and *trans* isomers of a cyclic saturated hydrocarbon. In such a case the forces acting in and between the molecules are quite similar and the differences in the physical properties of the compounds are due to a minimum number of differences in the forces acting. In this case it is evident that the isomer which has the greatest density and the greatest index of refraction has these properties as a result of its smaller molecular volume. It is equally true, if less obvious, that the smaller molecular volume leads to the higher boiling point<sup>8</sup> since the smaller molecular volume increases the magnitude of the dispersion forces which in turn leads to an increased heat of vaporization. The smaller molecular volume also requires the crowding together of the atoms within the molecule and, because of the internal repulsive forces encountered, a lower stability results. The rule stated is evidently a direct result of these effects and it may thus be determined what kinds of circumstances are required to cause the rule to fail.

An olefinic double bond may be considered in a formal sense as a two-membered ring and as such should also fit the rule. Consequently, the properties of some dozens of mono-olefinic hydrocarbons were considered<sup>9</sup> and, although in many cases the data are of insufficient accuracy to be definitive, no clear cut contradictions were found. Of particular interest are the isomers of

<sup>1</sup> G. EGLOFF, *Physical Constants of Hydrocarbons* (Reinhold, New York, N.Y. – J. S. FARADAY, *Encyclopedia of Hydrocarbon Compounds* (Chemindex, Manchester, 1945–52). – A. P. I. Tables, National Bureau of Standards.

<sup>2</sup> Account must be taken of the fact that some of the compounds listed as *cis* in the tables have since been shown to be *trans* and vice versa.

<sup>3</sup> A. SKITA and R. RÖSSLER, Ber. dtsch. chem. Ges. 72, 265 (1939).

<sup>4</sup> C. W. BECKETT, K. S. PITZER, and R. SPITZER, J. Amer. Chem. Soc. 69, 2488 (1947).

<sup>5</sup> S. F. BIRCH and R. A. DEAN, J. Chem. Soc. 1953, 2477.

<sup>6</sup> W. HÜCKEL, Ann. Chem. 533, 1 (1937).

<sup>7</sup> D. H. R. BARTON, J. Chem. Soc. 1953, 1027.

<sup>8</sup> T. W. RICHARDS, Trans. Faraday Soc. 24, 111 (1928).

<sup>9</sup> G. EGLOFF, *Physical Constants of Hydrocarbons* (Reinhold, New York, N.Y. – J. S. FARADAY, *Encyclopedia of Hydrocarbon Compounds* (Chemindex, Manchester, 1945–52). – A. P. I. Tables, National Bureau of Standards.

<sup>1</sup> K. VON AUWERS, Ann. Chem. 420, 84 (1920).