[3] Wilson, R. E., *Nature*, **234**, 406 (1971).
[4] Kríz, S., *Nature*, **245**, 36 (1973).
[5] Stotners, R., and Lucy, L. B., *Nature*, **236**, 218 (1972).
[6] Skulsky, M. J., *Soviet Astr.—AJ*, **15**, 606 (1971).
[7] Sahade, J., Huang, S. S., Struve, O., and Zebergs, V., *Trans. Am. Phil. Soc.*, **49**, 1 (1959).
[8] Batten, A. H., and Sahade, J., *Publ. astr. Soc. Pacif.*, **85**, 599 (1973).
[9] Hutchings, J. B., *Mon. Not., R. Astr. Soc.*, **155**, 55 (1970).
[10] Conti, P. S., and Leep, E. M., *Astrophys. J.* (in the press).
[11] Houck, T. E., *The Scientific Results from OAO-2* (edit. by Code, A. D.) 479 (NASA, 1972).
[12] Kippenhahn, R., and Weigert, A. Z., *Astrophys.*, **65**, 251 (1967).
[13] Danziger, I. J., Wallerstein, G., and Böhm-Vitense, E., *Astrophys. J.*, **150**, 239 (1967).
[14] Pringle, J. E., *Nature*, **243**, 90 (1973).
[15] Shakura, N. I., and Sunyaev, R. A., *Astr. Astrophys.*, **24**, 337 (1973).
[16] Wade, C. M., and Hjellming, R. M., *Nature*, **235**, 71 (1972).
[17] McCluskey, G. E., and Kondo, Y., *Astrophys. Space Sci.*, **10**, 464 (1971).

Behaviour of Comet Kohoutek (1973f)

OBSERVATIONS of Comet Kohoutek have revealed the presence of CH_3CN (ref. 1) and HCN (W. Huebner, private communication) in the coma and of H_2O^+ in the tail[2]; although predicted, H_2O was not observed[3].

The spectral identification of CH_3CN and HCN is the first direct support for the hypothesis first proposed by Wurm[4], of chemically stable 'parent molecules' for the less stable radicals and ions seen in the coma and the tail. Either of these molecules could be the parent molecule of CN, which is conspicuous in almost all comets at $\lambda \approx 3{,}883$ Å. Their radiative dissociation schemes are the following[5,6]:

$$CH_3CN + h\nu \rightarrow CH_3 + CN^* (\lambda \lesssim 2{,}160\ \text{Å}) \quad (1)$$
$$CN^* \rightarrow CN + h\nu (0\text{–}0 \text{ band emission near} \approx 3{,}883\ \text{Å})$$
$$HCN + h\nu \rightarrow H + CN\ (\lambda \lesssim 1{,}900\ \text{Å}) \quad (2)$$

These two molecules were among the earliest discovered in dense interstellar clouds[7]. This does not establish an interstellar origin for comets but seems suggestive of the environment in which comets, or more specifically their embryonic grains, condensed out of the gas phase. These two molecules are also among the most abundant products in the gas phase found in sparkings of simulated primitive planetary atmospheres[8].

The H^2O^+ (most probably formed by photoionisation of H_2O at wavelengths shortwards of about 984 Å; ref. 9); strongly suggests the presence of the latter as another parent molecule. Circumstantial evidence for the presence of H_2O as the dominant volatile component in the nucleus has been growing for some time. The strongest line of evidence has come from the recent ultraviolet and near violet observations of Comets Tago–Sato–Kosaka (1969g), Bennett (1969i), P/Encke, and now Kohoutek (1973f), all of which show strong emission from the two species H(Ly α) and OH(~3,040 Å) (refs 10, 11 and unpublished results from J. E. Blamont and M. Festau). Detailed models of the coma computed on the basis that H and OH are the photodissociation fragments of H_2O seem to explain rather well the observed Ly α brightness distribution[12,13] and the distortion of the isophotes[14]. Under typical cometary conditions with a large abundance of H_2O, other parent molecules would be present in the nucleus as clathrate hydrates, since these are thermodynamically more stable than their constituents[15]. Since the potential wells in which the 'guest molecules' are trapped in the H_2O ice lattice in the clathrate are very deep, they can be released only by the destruction of the 'host' lattice and consequently their vaporisation is controlled by the latent heat of vaporisation of H_2O. This explains the almost simultaneous appearance of all the major cometary emission bands (typically around 3 AU for most comets) although the volatilities of the assumed parent molecules differ by more than ten orders of magnitude, provided that the abundance (by number) of the H_2O molecules exceeds all others by about six to one. This is because the clathrate lattice can typically trap only one 'guest' molecule per six 'host' H_2O molecules. The large abundance of OH ($\gtrsim 90\%$ by number of all the radicals) observed in Comets Bester (1949k) (ref. 16) and Tago-Sato-Kosaka (1970g) (ref. 17) supports this view.

The behaviour of Comet Kohoutek cannot be explained by a pure clathrate nucleus with H_2O exceeding the other molecular species by more than 6 to 1. This is because an extensive dust halo was seen at a distance $R \gtrsim 4$ AU where the vapour pressure of H_2O or the clathrate would have been negligible[18]. A much more volatile species is required. Carbon monoxide, which is one of the most abundant molecules discovered in interstellar space and whose ion CO^+ is probably the most abundant species in cometary tails, is a likely candidate. Formaldehyde, another abundant interstellar species which may be a 'parent' for CO according to the scheme[5] $H_2CO + h\nu \rightarrow H_2 + CO (\lambda \lesssim 3{,}000\ \text{Å})$, is also a possibility. Methane is a not unlikely alternative. Indeed, the behaviour of Comet Kohoutek can be understood in terms of a nuclear model in which the H_2O exceeds the more volatile species by a factor less than 6:1 so that a fraction of these are not trapped in the clathrate lattice. It is also likely that these more volatile species were concentrated in an outer shell because of a slow outward diffusion. As the comet approached the Sun these volatile species would quickly evaporate around $R \approx 5$ AU, throwing out a dust halo which probably consists chiefly of clathrate hydrate grains, possibly also admixed with grains of the volatile species and more refractory, 'earthy' material. The extension (l) of this dust corona is not determined by the lifetime of the grains against evaporation at 5 AU because this would be too large for any reasonably sized grains (being about 5×10^{10} s for 10-μm grains). Rather it would be determined by their velocity. Taking $l \approx 10^4$ km and $v \approx 0.1$ km s^{-1} gives the time duration of mass ejection as $\approx 10^5$ s (≈ 1 d, which seems reasonable). Assuming that the injection rate of dust is β times that of the gas (Q_{gas}) and that the dust coma is optically thin, the 'effective cross section' of the dust coma for scattering of solar radiation is

$$A_c = \beta Q_{gas} \sigma_g\ \Delta t / m_g = \frac{3}{4}\beta \frac{(Q_{gas}\,\Delta t)}{(r_g\,\rho_g)} \quad (3)$$

where Δt is the duration of emission of the volatiles and σ_g, r_g, m_g and ρ_g are respectively the average cross section, radius, mass and density of a grain. Since $Q_{gas} = Z_{gas}\, m_{gas}\, A_n$, where A_n is the nuclear cross section, m_{gas} is the molecular mass of the voltaile and Z_{gas} is the vaporisation rate (molecules cm^{-2}s^{-1}), the ratio α of A_c to A_n is

$$\alpha = \frac{4}{3}\beta \frac{(Z_{gas}\, m_{gas})}{(r_g\,\rho_g)}\ \Delta t \quad (4)$$

Assuming that the volatile in question is CH_4 (which is representative of the highly volatile class and for which reliable data is available[19]), and putting $\Delta t \approx 10^5$s, $\beta \approx 0.1$, $r_g \approx 10$ μm, gives $\alpha \approx 40$. In spite of the overall uncertainty in this value arising from our guessed estimates, this shows that the 'effective cross section' at around 5 AU could have been one or two orders of magnitude larger than the nuclear cross section. Consequently, the earlier estimates of the radius could have been too large by a factor of about three to ten, accounting for the later disappointment.

If the highly volatile material involved is small, this activity will quickly cease and a much less volatile cometary nucleus consisting of clathrate hydrates will be exposed, which will then behave in a 'normal' way after the early 'anomalous' brightening

Comet Kohoutek is by no means unique in its behaviour and five out of a set of about 50 long period comets seem to show anomalous brightenings in $4\ \mathrm{AU} \leqslant R \leqslant 5\ \mathrm{AU}$ (ref. 20). A much larger sample (about 75% of a total of 79 comets passing perihelion in a period of 40 yr) exhibited flare activity at smaller heliocentric distances, often repeatedly[21,22], and indeed a significant fraction of all long period comets may be first observed during such flares[23]. These flares, as well as the periodic outbursts from P/Schwassman–Wachmann 1, which moves in a nearly circular orbit with perihelion distance ≈ 5.5 AU, can be explained in terms of pockets of the highly volatile material contained within the clathrate lattice, being exposed to solar radiation from time to time as the overlying material evaporates. Other explanations of this phenomenon have been suggested[24,25] but they are less direct.

Any attempt such as this to explain the differences of cometary behaviour in terms of differences in composition runs into the difficulty of having to explain why such differences in composition should exist, and this can only lead to further speculation because next to nothing is known about the spatial regions and therefore the physical and chemical environments in which comets condensed[26]. But we require only very small differences in chemical composition to explain very different behaviour. A comet whose volatile component contains 85% H_2O molecules by number will behave in a 'normal' way, whereas one which has only 84% H_2O molecules by number will flare at a large heliocentric distance ($R \geqslant 5$ AU) and then fizzle out, like Comet Kohoutek. Such small differences in chemical composition could easily be attributed to random statistical fluctuations. This may also be the difference between genuinely 'new' comets coming into the inner Solar System for the first time and those that have come in at least once before.

This work was supported by the Planetology Program Office, Office of Space Sciences, National Aeronautics and Space Administration.

D. A. MENDIS
W-H. IP

Department of Applied Physics and Information Science,
University of California, San Diego,
La Jolla, California 92037

Received March 8, 1974.

[1] Ulich, B. L., and Conklin, E. K., *IAU Circ.* 2607, (1973).

[2] Herzberg, G., and Len, H., *IAU Circ.* 2618, (1974).

[3] Ip, W-H., and Mendis, D. A., *Nature*, **245**, 197 (1973).

[4] Wurm, K., *Mitt. Hamburger Sternw.*, **8**, No. 51 (1943).

[5] Calvert, J. G., and Pitts, J. N., *Photochemistry*, 485 (Wiley, New York, 1966).

[6] Rank, D. M., Townes, C. H., and Welch, W. J., *Science*, **174**, 1083 (1971).

[7] Litvak, M. M., in *Atoms and Molecules in Astrophysics* (edit. by Carson, T. R., and Roberts, M. J.), 2d (Academic Press, London, 1972).

[8] Sagan, C., *Nature*, **238**, 77 (1972).

[9] Hudson, R. D., *Rev. Geophys. Space Phys.*, **9**, 305 (1971).

[10] Code, A. D., and Lillie, C. F., *IAU Circ.* 221, (1970).

[11] Bertaux, J. A., Blamont, J. E., Festau, M., *Astr. Astrophys.*, **25**, 415 (1973).

[12] Mendis, D. A., Holzer, T. E., and Axford, W. I., *Astrophys. Space Sci.*, **15**, 313 (1972).

[13] Ip, W-H., and Mendis, D. A., *Astrophys. Space Sci.*, **26**, 153 (1974).

[14] Keller, H. U., *Mitt. Astr. Gesellschaft*, **30**, 143 (1971).

[15] Delsemme, A. H., and Wagner, A., *Planet. Space Sci.*, **18**, 709 (1970).

[16] Arpigny, C., *Acad. Belgique Cl. Sci.*, **35**, 5 (1965).

[17] Code, A. D., and Savage, B. D., *Science*, **177**, 213 (1972).

[18] Biermann, L., *Nature*, **246**, 400 (1973).

[19] Delsemme, A. H., and Miller, D. C., *Planet. Space Sci.*, **19**, 1229 (1971).

[20] Pittich, E. M., *The Motion, Evolution of Orbits, and Origin of Comets* (edit. by Chebotarev, G. A., and Kazimirchak-Polonskaya, E. I.), 283 (Reidel, Dordrecht, 1972).

[21] Vsekhsvyatskii, S. K., *Nature et Origin des Comets* (edit. by Swings, P.), 53, (Institut Astrophysique, Cointe-Sclessin, Belgium, 1966).

[22] Vsekhsvyatskii, S. K., *Physical Characteristics of Comets* (Israel Program of Scientific Translations, Jerusalem, 1964).

[23] Richter, N. B., *Nature of Comets* (Methuen, London, 1963).

[24] Donn, B., and Urey, H. C., *Astrophys. J.*, **123**, 339 (1956).

[25] Eviatar, A., Joseph, J. H., and Dryer, M., *Cosmic Electrodynamics*, **1**, 239 (1970).

[26] Alfven, H. A., and Mendis, D. A., *Nature*, **246**, 410 (1973).

Monotonic evolution of Boltzmann's *H* in weakly coupled gravitational systems

GASES with gravitational interactions are expected to evolve away from a state of uniform density and temperature[1,2]. Such behaviour has been strikingly confirmed by numerical experiments on small gravitational systems[3].

We point out here that this evolution does not contradict the criterion:

$$\mathrm{d}H/\mathrm{d}t < 0 \qquad (1)$$

Indeed this criterion can even be proved. Here,

$$H = N\int \mathrm{d}\mathbf{v}\ \psi(\mathbf{v}) \ln \psi(\mathbf{v}) + \text{constant} \qquad (2)$$

is Boltzmann's H, ψ is the velocity distribution of particles with equal masses m. The weak coupling theory of Prigogine and Severne[4,5] leads to a criterion of evolution of the form defined by equation 1, mainly as a byproduct of the simultaneous increase of random kinetic energy and negative correlational potential energy[6]. The criterion is illustrated in Fig. 1, which, following Miller[3], is a schematic plot of the evolution of the random kinetic energy and Boltzmann's H. They do not approach a limiting value. The approach of the velocity distribution towards a Maxwellian one is deflected by an instability of the Maxwellian distributions themselves.

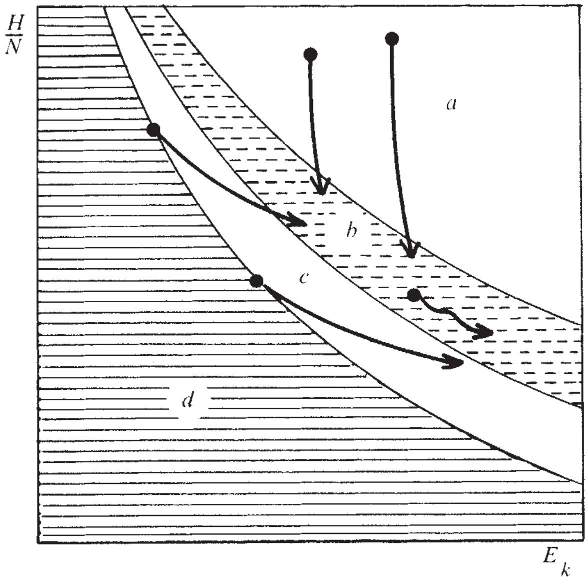

Fig. 1 The monotonic increase in mean kinetic energy per particle, E_k and the monotonic decrease in Boltzmann's H. The size of regions b and c may be much smaller than shown. The line between regions c and d represents Maxwellian velocity distributions ($2E_k\mathrm{d}H = -3N\mathrm{d}E_k$). Region d contains no allowed distributions. The solid circles represent hypothetical distributions at time t and the arrows show the direction of evolution of H and E_k from these points. Region a is dominated by the usual relaxation of H because of weak binary interactions. Region c is dominated by the kinetic energy production and associated negative potential energy production. The H quantity also decreases there, primarily because of increasing disorder in velocity space as a result of the heating. The evolution in region b is less rigorously established, and the region has not been shown to have boundaries independent of moments of the velocity distribution other than H and E_k. It has, however, been shown that $\mathrm{d}E_k/\mathrm{d}t > 0$ even in region b, and therefore $\mathrm{d}H/\mathrm{d}t < 0$ holds everywhere, at least over a period of time.

The Maxwellian is unstable because of distortions associated with the creation of spatial order (ref. 7, and M. J. H., not yet published). This could be crudely described as a dissipative 'flow of entropy' (and of energy) from spatial coordinates to velocity coordinates. Some local order in velocity space develops and is maintained as a byproduct, in spite of the increase in overall dispersion of the velocities.