

an increase of less than a factor of 10 in $1/\text{Xe}$ ratio in a melt. This model can therefore produce the observed present-day $1/\text{Xe}$ ratio of Mars from chondritic starting material.

Our model agrees with an earlier assertion⁷ that iodine will have been incorporated into martian crustal rocks formed early in the planet's history, whereas xenon was outgassed and lost. The sequestering of ^{129}I -derived ^{129}Xe into the martian crust in our model is also consistent with an earlier suggestion¹⁸ that the easiest way to produce SPB xenon is to fractionate xenon from average carbonaceous chondrites and then add ^{129}Xe . The

fractionation of this xenon could occur during late accretion, perhaps by hydrodynamic escape¹⁹, or during or immediately after late, heavy bombardment by some other mechanism that also depends on mass. The addition of ^{129}Xe would occur by slow release from the crust over geologic time. Outgassing of martian surface rocks following the loss of a substantial portion of the martian atmosphere is consistent with enrichment of ^{40}Ar in the martian atmosphere⁵ ($^{40}\text{Ar}/^{36}\text{Ar} = 3,000$ for Mars, 295 for Earth), which resulted from the release of ^{40}Ar produced by decay of ^{40}K over geologic time. □

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Paradoxical behaviour of mechanical and electrical networks

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WE describe here a network of strings and springs in which cutting a string that supports a weight results in a rise of the weight at equilibrium. In an analogous electronic circuit of passive two-terminal devices (resistors and Zener diodes), adding a current-carrying path increases the voltage drop across the circuit. These systems are mechanical and electrical analogues of a paradox of congested traffic flow^{1,2}. Along with similar hydraulic and thermal analogues, they show how non-intuitive equilibrium behaviour can arise in physical networks made up of classical components.

In the network of strings and springs shown in Fig. 1a, one end of a spring is attached to a fixed support, and the other end to a string of length $L = \frac{1}{2}$ m. One end of another identical spring is attached to the free end of the string, and a weight is attached to the free end of the second spring. A back-up string joins the support to the upper end of the second spring, and an identical back-up string joins the lower end of the first spring to the weight. These back-up strings are long enough to be limp when the linking string of length $L = \frac{1}{2}$ m is intact.

Assume the strings are massless and perfectly inelastic, and that the springs are massless, ideally elastic and have zero unstretched length. Assume each spring has a spring constant equal to k so that its extension x is related to the applied force F by $F = kx$. For simplicity, we will take $k = 1$. If the weight exerts a force of $\frac{1}{2}$ N, the extension of each spring will be $\frac{1}{2}$ m. Therefore the distance from the support to the lower end of the linking string is $\frac{1}{2} + \frac{1}{2} = 1$ m. The distance from the upper end of the linking string to the weight is the same. The length of the two safety strings is chosen as 1 m so that they hang limply. The distance X from the support to the weight is $\frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1\frac{1}{2}$ m.

Intuition (ours and that of other people we have asked) suggests that if the linking string were cut, the weight would drop and the distance X would increase. In fact, the opposite is true. If the linking string is cut, the network becomes as shown in Fig. 1b. The safety string attached to the support and the lower spring attached to that string now bear half the weight. The upper spring and the safety string attached to the weight bear the other half of the weight. Therefore the extension of each spring is $\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$ m, and the distance X from the support to the weight is now $1 + \frac{1}{4} = 1\frac{1}{4}$ m, less than before. At equilibrium, the weight is higher than before. Directionality is irrelevant. The phenomenon would be the same if the network were hung upside down. (When the strings and springs are massless, even the initial transient motion of the weight is upward just after the string is cut.) Of course, at equilibrium, the whole network has less potential energy after the string is cut than before.

Suppose the length of the cross-linking string varies smoothly from 0 to 1 m, while all other elements of the network remain as in Fig. 1a. Figure 2 shows the equilibrium distance from the support to the weight as a function of the length L of the cross-linking string. For any L between 0.25 m and 0.75 m, the weight would be higher (the distance X from the support to the weight would be smaller) if the cross-link were cut.

An electrical analogue of the paradoxical mechanical network may be constructed by associating current (I) with force and voltage (V) with displacement. A spring with zero rest length (which obeys $F = kx$) thus becomes a resistor ($I = V/R$), with resistance R analogous to the inverse of the spring constant, $1/k$. A string (of constant length x , for any $F > 0$) becomes a Zener diode ($V = V_Z$, for any $I > 0$), with its characteristic Zener voltage V_Z analogous to the string's length. These ideal circuit elements can be realized fairly accurately in practice³.

Figure 3a shows the resulting electrical analogue of Fig. 1b, drawn as a Wheatstone bridge. To match the elastic springs and inelastic strings of Fig. 1b, we will consider 1- Ω resistors and 1-V Zener diodes in the outer legs (unrealistic values in practice, but convenient for illustration). A current of $I = \frac{1}{2}$ A flowing into the top terminal divides equally between the two paths, producing a voltage drop of $V = \frac{1}{2}IR_4 + V_{Z1} = \frac{1}{2}IR_2 + V_{Z2} = \frac{1}{2} + 1 = 1\frac{1}{2}$ V. Providing an additional conducting path across the bridge in the form of a $\frac{1}{2}$ -V Zener diode (analogous to the cross-linking string of length $L = \frac{1}{2}$ m) produces the circuit of Fig. 3b, in which all the current flows through R_2 , Z_3 and R_4 , and the voltage drop has increased to $V = IR_2 + V_{Z3} + IR_4 = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 1\frac{1}{4}$ volts. No current flows through the 1-V Zener diodes, because the

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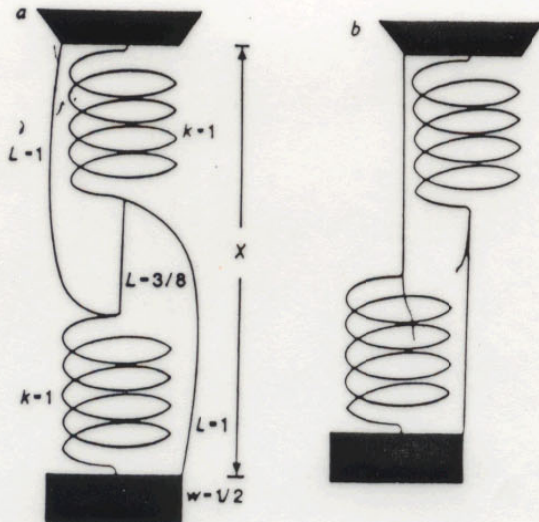


FIG 1 Mechanical network. Springs have zero unstretched length and spring constant $k=1$. Strings are inelastic. The string that links the two springs has length $\frac{3}{8}$ m. Both safety strings have length 1 m. The weight exerts a force of $\frac{1}{2}$ N. a. In the initial network, both safety strings are limp and the distance X from support to weight is $1\frac{1}{2}$ m. b. After the linking string is cut, the weight is higher at equilibrium; the new distance from support to weight is $1\frac{1}{4}$ m.

voltage drop across each is only $\frac{1}{2}$ V. Adding a new current-carrying path, while leaving all previous paths in place, thus decreases the conductivity of the overall two-terminal network.

As in the mechanical network, directionality is irrelevant. Although unidirectional Zener diodes were used in this example, they could be replaced with bidirectional Zener diodes³. The current paths are set by the sign of the forcing function (the applied current) and the circuit topology, and would be identical to those of Fig. 3. In the circuit with bidirectional diodes, the applied current could be of either sign, with similar results (analogous to an interchange of weight and support in the mechanical model).

For the topology of the Wheatstone bridge, it is easy to see under what conditions the paradox occurs. In Fig. 3b, let both

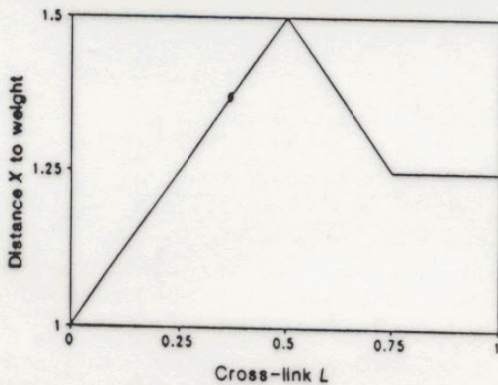


FIG 2 Distance X from the support to the weight, as a function of the length L of the cross-linking string. For any L between $\frac{1}{2}$ and $\frac{3}{4}$ m the distance from the support to the weight will be smaller if the cross-link is cut. The dot shows the position of the network in Fig. 1a.

the current I (A) and the voltage V_{Z3} (V) of the bridging Zener Z_3 , be variable positive numbers. Then a paradoxical change in voltage drop occurs if $1 - 3I/2 < V_{Z3} < 1 - I/2$. The right-hand inequality guarantees that current flows through Z_3 . The left-hand inequality guarantees that the conductivity is reduced by adding the additional path. As $V_{Z3} \geq 0$, I must be less than 2 A. The maximum ratio of the voltage drop with the cross-bridge to the voltage drop without the cross-bridge (or distance X , for the mechanical analogue) is $\frac{3}{2}$, and occurs when $I = 1$ and $V_{Z3} = 0$ (the voltage drop is 2 V with the bridge, $1\frac{1}{2}$ V without it).

An arbitrary two-terminal electrical network with a fixed current source in which all branches contain only strictly linear resistors (those for which $V = IR$) cannot produce this paradoxical behaviour⁴⁻⁶. Consequently neither can a mechanical network in which all elements are massless, ideally elastic springs with zero unstretched length. These general results add force to the surprise produced by the examples in Figs 1 and 3.

Additional paths may cause reduced flow in other electrical circuits in ways that are not counter-intuitive. The circuit in Figure 4, for example, consists of a bipolar transistor and one resistor. When the dashed path is open, or not connected, the circuit conducts heavily for any applied voltage greater than ~ 1 V (or, equivalently, any applied current results in a voltage drop of ~ 1 V). If the dashed path is connected (a conducting path is added), the transistor no longer conducts, and the circuit behaves like a single resistor, R ; the conduction across the circuit is thus greatly reduced. This behaviour is hardly paradoxical, owing to the presence of an active three-terminal device (the transistor). By contrast, the circuits of Fig. 3 use only passive two-terminal devices, and there the increase in voltage drop with an additional current path seems genuinely counter-intuitive.

The networks in Figs 1 and 3 are analogous to a hydraulic

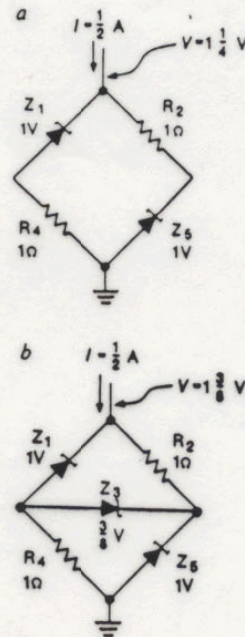


FIG 3 Electrical network of ideal components. a. Initially, current flows symmetrically through left and right branches, and the voltage drop from source to ground is $1\frac{1}{4}$ V. b. When a $\frac{3}{8}$ -V Zener diode is introduced across the network, the current through the 1-V Zener diodes drops to zero and all current flows through the 1- Ω resistors and the $\frac{3}{8}$ -V Zener diode, producing a larger voltage drop from source to ground of $1\frac{3}{8}$ V.

network carrying an incompressible fluid in which the inelastic strings or Zener diodes are replaced by constant-pressure-difference valves (sometimes called pressure-relief valves or safety valves) and the elastic springs or linear resistors are represented by tubing of appropriate length with incompressible viscous (Poiseuille) flow; fluid flow is then analogous to weight or electrical current, and pressure difference is analogous to extension or voltage drop⁷. In an analogous thermal network, heat flow corresponds to weight or current, and temperature difference corresponds to extension or voltage drop⁸.

These physical paradoxes are closely connected to a paradox in traffic flow discovered by Braess¹. In an idealized traffic network, each individual seeks a minimal-cost (or shortest) path from a point of entry to a point of exit. In an uncongested network, the choices of paths through the network made by different individuals do not affect one another. Adding uncongested routes to an uncongested network can only lower, or at worst not change, the time individuals require to travel through the network from a source to a destination. A congested network differs from an uncongested one in that, for at least one arc of a congested network, the cost (per person or vehicle) of travel along that arc strictly increases with increasing traffic flow. Braess^{1,2} discovered a congested transportation network such that, if a link is added and all individuals seek their best possible route, at the new equilibrium the cost of travel for all individuals is higher than before.

Braess's paradox (additional capacity leading to more costly travel for all) occurs both in general transportation networks^{9,10} and in a queuing network¹¹. Thus Braess's paradox is not a peculiarity of the mathematical formalism Braess used to describe a transportation network, but appears to be a more general property of some congested flows. Transportation and queuing networks are special examples of non-cooperative games, for which a general analogue of Braess's paradox holds¹²; in the language of game theory, Nash equilibria of non-cooperative games are generically Pareto-inefficient.

Braess's original model translates to a mechanical network similar to Fig. 1, with each inelastic string replaced by an inelastic string in series with a spring; or, analogously, to an electrical circuit similar to Fig. 3, with each Zener diode replaced by a Zener diode in series with a resistor. The translations among transportation networks, mechanical networks, electric circuits and hydraulic networks are exact because there is conservation at every node (traffic in equals traffic out, mechanical force upward equals mechanical force downward at equilibrium, and so on) and because different paths from one node to another, if used, must have equal cost (travel time, stretch, voltage drop or pressure drop). Analogues of Braess's paradox should also exist in continuous representations of systems that obey Kirchhoff's laws.

These mechanical and electrical analogues of Braess's paradox illustrate the possibility of counter-intuitive equilibrium

behavior in physical networks when the load imposed on an arc affects that arc's behaviour (stretch or voltage drop, in these examples). The task remains of specifying the general conditions under which such paradoxes can occur, for general network topologies and broad classes of components, possibly including nonlinear ones. The examples presented here suggest caution in assuming that physical networks will behave as normally expected when paths or components are added. □

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Preparation and structure of the alkali-metal fulleride A_4C_{60}

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SUPERCONDUCTING K_3C_{60} (ref. 1) has been shown² to have an intercalated face-centred cubic (f.c.c.) structure, and other A_xC_{60} compounds (where A is K, Rb or mixtures of K, Rb and/or Cs) form an isostructural series with superconducting transition temperatures up to 31.3 K (ref. 3). Recently we reported⁴ ¹³C NMR studies of K_xC_{60} for $x < 3$, and concluded that the system contained two phases ($x = 0$ and $x = 3$) for $0 < x < 3$. Here we report an investigation of A_xC_{60} in the range $3 < x < 6$ and find evidence for an additional phase at $x = 4$. In contrast to f.c.c. A_3C_{60} (refs 2, 3) and body-centred cubic A_6C_{60} (ref. 5), A_4C_{60} (where A is K, Rb, Cs) has a body-centred tetragonal structure. We show that all of the experimentally observed phases of A_xC_{60} can be predicted solely on the basis of electrostatic considerations. We have found no evidence for superconductivity in A_4C_{60} .

Rb_4C_{60} was prepared by reaction of stoichiometric quantities at 225 °C for three days followed by 400 °C for one week in sealed, evacuated Pyrex tubes. K_4C_{60} was prepared by thermal de-intercalation of K_6C_{60} by heating in an evacuated Pyrex ampoule for one week in a thermal gradient with the K_6C_{60} at 550 °C and the cold end at room temperature. After de-intercalation, X-ray diffraction showed the material to be single-phase body-centred tetragonal (b.c.t.). For Cs_3C_{60} , the b.c.t. phase has been seen thus far only in two-phase samples prepared by reaction of material with nominal composition Cs_3C_{60} .

Representative $Cu K\alpha$ X-ray powder patterns of K_xC_{60} in sealed glass capillaries are shown in Fig. 1 for $x = 0, 3, 4$ and 6. C_{60} and K_3C_{60} can be indexed as f.c.c. with the lattice parameters shown^{2,3}, whereas K_6C_{60} is body-centred cubic (b.c.c.)⁵. A_4C_{60} is neither b.c.c. nor f.c.c., but instead can be indexed with a b.c.t. unit cell with lattice parameters of $a = 11.886(7)$ and $c = 10.774(6)$ for K_4C_{60} , and $a = 11.962(2)$ and $c = 11.022(2)$ for

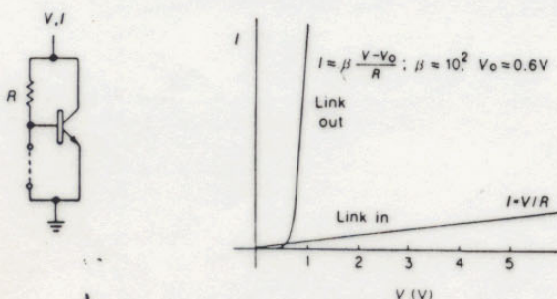


FIG. 4 A less surprising two-terminal electrical network in which an added current path (dotted) causes less current to flow from source to ground. The transistor acts as a switch.