THE BIG IDEA: Marcus Theory

Marcus Theory helps scientists understand better what actually goes on in the most fundamental biological and chemical processes such as respiration, metabolism, detoxification, photosynthesis and corrosion.

Before 1956, many scientists marvelled at a theory by American chemist Bill Libby, who argued that when electrons jumped from one molecule to another, these molecules would react to the jump by changing their surroundings in some way. The problem with that view: to do so, the molecules would spend more energy than they had, which violated the natural law that energy in a system should be conserved.

Then, in 1956, theoretical chemist Rudolph Marcus went to work on this conundrum. He had just completed some research on gas phases, and was looking for a new field to study.

As it happened, he got interested in the behaviour of molecules in liquid, which led him to Professor Libby's theory. Within a month, he discovered that, contrary to the view that these molecules reacted to the jump, it was actually the molecules that prepared the electrons for the jump.

The molecules did so, with the help of heat and the environment around them, by working themselves into such a state that the electrons had energy to leap forward fast.

This became known as Marcus Theory, which has since helped scientists make headway on such endeavours as:

- Finding ways to make solar cells harvest energy from sunlight more efficiently, such that the cells generate the highest currents with the least effort;
- Finding ways to sense DNA damage more acutely and repair that well; and
- Finding ways to overcome breakdowns in essential biological functions, such as metabolic or detoxification processes.

Piecing together the electron puzzle

Thanks to Nobel chemistry laureate Rudolph Marcus' brainwave, scientists are better able to explore ideas such as targeted DNA repairs and even artificial leaves

By CHEONG SUK-WAI
SENIOR WRITER

SOME have likened the randomness of life to a box of chocolates whose nutty, creamy or fruity centres are revealed only when you bite into them.

But random though life may be, it is actually sustained by a well-ordered chain of reactions, set off by tiny buzzy sub-particles called electrons that jump from one molecule to another and another until it completes its purpose.

So, for example, when the sun shines on a plant, the energy from its rays excites the plant's chlorophyll, or pigment, molecules. These wildly vibrating molecules give their electrons the bounce they need to shoot over to another place.

Such jumping is called electron transfer and results in chemical reactions, that is, it creates new chemicals which then react with other chemicals. An example of such a reaction is when iron rusts, because when electrons bounce off one type of iron particle onto another, the first particle loses electrons and is thus oxidised, or rusted.

Crucially, electron transfer is also what keeps every living thing alive, as it is the way in which a plant or person converts sunlight or food into energy. So it is that waves of leaping electrons enable such vital processes as respiration, metabolism, photosynthesis and detoxification.

But up till the mid-20th century, nobody knew why electrons sometimes jumped faster and sometimes slower. It was crucial that scientists understood this if they were to control the impact of chemicals on life.

Then, in 1956, Canadian-born chemist Rudolph Marcus cracked how to explain the rate of electron transfers – in just one month, after reading an article in his local library by an American chemist named Bill Libby. Professor Marcus was then all of 33, teaching in the little-known Polytechnic Institute of Brooklyn in New York and restless for a new field to study. That had him reading up on how molecules behaved in liquid, which led him to Prof Libby's work.

Professor Marcus was in town late last month to attend a three-day conference at the Nanyang Technological University (NTU) to commemorate his 90th birthday this year. He has been teaching and doing research at the California Institute of Technology (Caltech) since 1978, and is now also a visiting don at NTU.

Recalling his response to Prof Libby's article, Prof Marcus says: "I was so excited about it because Bill had applied a 1920s theory to explain how molecules absorbed light to explain the rate of chemical reactions instead.

"My excitement forced me to think harder about it because instinctively, I felt that while his approach was right, his back-of-the-envelope calculations were not."

Prof Libby, who later won the Nobel Prize in Chemistry for radiocarbon dating, argued that when electrons jumped, the environment around them adjusted afterwards. But, to Prof Marcus, such a view meant that electron transfers could happen only when there was light, which violated the natural law that systems could not spend more energy than they already had.

Prof Marcus' brainwave was realising a molecule and its environment would adjust first to put themselves in such a state that gave electrons enough energy to jump across successfully.

He hit on this by experimenting with particles in liquid. Asked why others could not see what he saw, he says it boiled down to his insistence on always picturing ideas in physical, not abstract, detail.

"I regard Nature as real and so there has to be an explanation about what you observe of it. You may or may not find the explanation, but there has to be one."

At that time, the reigning theory on electron transfer was that derived in 1935 by American scientist Henry Eyring and his team. Prof Marcus recalls: "Eyring's theory said, 'Here are a cluster of different buildings and we can understand some general things about them'. "What I did in 1956 was say, 'I'm going to look into great detail at each type of building in this cluster and get new results.' "

He published his findings in two papers soon after, but it took his fellow scientists another 30 years to test and prove his big idea, which is now known as Marcus Theory and which won him the 1992 Nobel Prize in Chemistry.

Marcus Theory is considered so seismic that Prof Mark Ratner of Northwestern University insists that it is "the theory of everything". To that, Prof Marcus says: "Well, that's very sweet but as it turns out – and this is where luck comes into it – there happens to be quite a few processes in life which are electron transfers such as respiration and photosynthesis.

"So Nature had everything to do with it, and the fact that my theory can be widely applied is a bonus!"

He has given scientists a basis to understand deeply what they were observing in so many scientific processes and has also egged them on to solve puzzles such as finding new, clean and abundant sources of energy. So they are now able to explore seriously such ideas as:

- How to make and improve on solar-powered panels and batteries;
- How to make artificial leaves which can mimic the process of photosynthesis and turn sunlight into, say, liquid fuel to power cars. This would eliminate the expensive option of converting foods such as corn and soya beans into fuel as sunlight is free and also the most carbon-neutral energy source there is; and
- How DNA in a genome is damaged, and how cells sense the damage and repair it. This helps treat, say, skin cancer in which one's DNA is damaged by ultra-violet rays.

Prof Marcus says that it is "a great, unconscious joy" for him to be still around to see how his big idea has inspired so many innovations. It is a rare vantage point indeed for this sanguine, self-effacing man, who, from a very young age, enjoyed building things with his child's Erector construction set and structuring his thoughts "because structure makes for better theory".

But, he is quick to point out that the world does not conform to structure: "Most of the big developments are accidental; you can't structure news that breaks."

Born in Montreal in 1923, he is the only son of an all-round athlete and a "very spiritual" pianist. But he looked to his father's two brothers, who were doctors, and his great-uncle, Swedish don Henrik Steen, for career inspiration.

The widower with three sons secured his PhD in chemistry from Canada's McGill University in 1946 and did post-doctoral research at the National Research Council of Canada until 1949, when he moved to the United States to research and teach at a host of under-the-radar tertiary institutions.

He became a US citizen in 1960 because it was a "scientific beehive and so where the jobs were" and, in 1978, was appointed to his present position at Caltech.

Of science today, he muses: "I wish there weren't all this focus now on wanting immediate results.

"For the most part, I think that's unfortunate because some of the better things that have come out of science were just out of intellectual curiosity, and not for the intention of applying the science."

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Cheong Suk-Wai meets a thinker in this fortnightly column, which alternates with The Big Read, in which she reviews books on ideas

Prof Marcus says his ability to see what others could not, boiled down to his insistence on always picturing ideas in physical, not abstract, detail. PHOTO: NTU

Rudolph Marcus on...

HOW TO SUCCEED IN SCIENCE

"Focus on having fun at it, and don't think of big prizes. It never occurred to me to win the Nobel."

HOW WINNING THE NOBEL PRIZE CHANGED HIS LIFE

"It's made it more difficult because I now have to go to meetings that aren't primarily about science and do interviews. My life may be more interesting now, but it's not easy."

WHAT HE HAS ACHIEVED SINCE HIS NOBEL WIN

"This may be a defect, but I've worked on so many things, it's hard for me to remember most of them."

WHAT ABOUT LIVING FOR 90 YEARS GLADDENS HIM

"I'm glad of the cry for justice in many countries. I'm glad when another illness is conquered. And I'm glad when younger people make unusual discoveries – even though I had nothing to do with it."

WHAT HE MISSES ABOUT CANADA

"There are fewer guns there!"

THE IDEA OF GOD

"Some people would like to believe it and that's fine. I'm comfortable with whatever makes them comfortable."

WHY HE DOES NOT BELIEVE IN GOD

"Because I can't do experiments to test that sort of knowledge. So I'm willing to live with not knowing the answer to every fundamental question."

WHAT GIVES HIM THE MOST PLEASURE THESE DAYS

"Skiing – the thrill of going down amid breathtaking scenery and with the wind against my face."

HEAR IT

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PROF RUDOLPH MARCUS tells of what he wishes humanity understood better about life

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THE BIG IDEA IN HISTORY: Electron transfer

THE man who really got the ball rolling on understanding electron transfer was poetry-loving Dutchman Jacobus Henricus van't Hoff, who had defied his doctor father by studying chemistry instead of medicine.

In 1884, Mr van't Hoff published his observations that when one upset the state of equilibrium – that is, a state of unchanging pressure, temperature and other properties – in a system of particles either by heating or cooling it, that system would always oppose the temperature change in a bid to restore equilibrium.

So when the temperature was turned up, the particles in the system would absorb the extra heat and cool down, and vice-versa.

This principle of thermodynamics helped garner him the first Nobel Prize in Chemistry in 1901, and enabled scores of scientists after him to found the field of physical chemistry. Among them was his Swedish peer and fellow Nobel laureate Svante Arrhenius, who in 1889 hit upon his equation, which would be named after him, that, among other things, showed that the rate at which electrons jump from one particle to another depends on how high the temperature and energy around it are.

Then, in 1935, scientists Henry Eyring, M. G. Evans and Michael Polanyi took Dr Arrhenius' findings further by developing a theory about how fast, or slow, certain elementary chemical reactions were.

Professor Rudolph Marcus built on what is called their "transition state theory" to arrive at his own theory in 1956. It helped that by then, science had developed new experiments and tools, including lasers, to understand better where and how electrons jumped from one particle to another.

THE BIG IDEA IN ACTION: When divorce is a good thing

MANY scientists today consider Marcus Theory to be one of the biggest ideas in chemistry after World War II.

This big idea has been particularly enlightening in attempts to tap sunlight as a clean energy source, also known as solar energy conversion, says Professor Maria-Elisabeth Michel-Beyerle of the Nanyang Technological University's School of Physical and Mathematical Sciences.

Prof Michel-Beyerle, 77, specialises in electron transfers in photosynthesis, or transforming sunlight into sugar and water, and other biological systems such as respiration.

A plant sucks in energy from the sun through its antenna made up of chlorophyll, or pigment, molecules. When these pigment molecules absorb sunlight, the energy from that light is channelled to another part of the plant called the reaction centre. At this hub, the energy from the absorbed light excites the molecules' electrons such that they lurch from one particle to another. This electron-jumping leads to a "charge separation", because once an electron leaps from one molecule to another, the first molecule is left with a "hole" from the electron loss. Prof Michel-Beyerle likens this charge separation to a train hurtling downhill.

Finally, certain structures within the plant recombine the separated charges, and this recombination produces the energy that plants can use and store. This move, she says, is akin to a train going backwards.

Here is where it all gets really interesting. Characterising the electron jumps and their later recombination as a marriage, she likens charge separation to a divorce, and stresses: "To convert light to usable energy most efficiently, you need the divorce to be quicker than the marriage, that is, the charges must split faster than they merge."

But the really stunning part of Marcus Theory, she adds, is that it explains why trying to speed up the train hurtling downhill by introducing more energy into it for faster charge separation does not work. That is because the entire chemical system cannot "digest" the added impetus and would actually slow down. "It is really counter-intuitive, but this is what makes Marcus Theory ingenious," she notes.

Thanks to the theory, she and her colleagues – led by Prof Subodh Mhaisalkar – at the Energy Research Institute @ NTU, better known as Eri@n, have since found a groundbreaking way to convert energy more efficiently, using what she describes, for simplicity's sake, as "a black film on which light is shone" to test the maximum level of energy that can be harvested from sunlight.