Fuel Cells, Engines and Hydrogen
An Exergy Approach

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This book is dedicated to my wife, without whom it could not have been written. The dedication poem below is written in a mixture of Buchan Claïk (Buchan dialect) and Lallans (Lowland Scots), as befits a marriage between a husband from Edinburgh, but of Glaswegian upbringing, and a wife from Aberdeen. In Buchan Claïk loons (m) and quines (f) are marriageable young people.

My Bucksburn Quine

O Mary, it’s lang syne we click’d,
While touching over teacups,
I tak’t ye fae a jilted loon,
Sair sick doon in his stommick.

My Bucksburn quine had black dark hair,
That spark’d a’twixt the bed sheets,
Glintin’ the way tae lovers rites,
That spritely gint the hert leap.

The potter’s clay from high she thumps,
Upon the caring plaster,
Wi’ micht an main, tae get it richt,
Tae form, and fire, and gloster.

My Buchan quine, ma ain guidwife,
In the game o’life, a winner,
O’er wrongs and rights, and deil made plights,
That yowt the heid’s wee spinner.
A doughty fechter in the fight,
Wi’ posture, and good balance,
An’ shak’, will she, the hand o’ God,
When life’s brief flash is darkened.

Our bairns, and bairns’s bairns are fair,
A trace we’ll leave behind us,
Meantime the bond o’blood is there,
That joins and keeps and twines us.

A fortun’d, fair starred man am I,
Health’s, wealth beyond conception,
And love thy neighbour as thy self,
Precludes the deil’s pre-emption.
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At first glance, the detailed study of how equilibrium thermodynamics may be used to analyse fuel cells seems far removed from the mainstream of fuel cell development. Fuel cell developers are necessarily caught up in a trade where increased irreversibilities are embraced in return for reductions in capital cost and comparisons are made with heat engines from the flawed but familiar mindset of energy and heating values. However, such perspectives, comfortably close though they are to current thinking, ignore not only the full potential of fuel cells to impact the exchange of useful work but also the benefit to be gained from a fresh approach to the engineering of fuel cells from a fundamental perspective.

The study of seemingly abstract aspects of quantum mechanics and solid state physics led paradoxically not only to semiconductor devices themselves but also to fresh insights into how pragmatism could be used to engineer these devices into even more useful forms that could be connected in a highly integrated fashion and dramatically reduced in size. Fresh study of the detailed thermodynamics of fuel cells is at the very least a valuable intellectual exercise for any practitioner in a fuel-cell-related discipline. With a little historical reflection, few could ignore that it might lead to further insights that could directly benefit the pragmatic development of commercially saleable fuel cells.

In Mr Barclay’s latest work we see not only a more comprehensive equilibrium thermodynamics analysis than in his previous works but also a much awaited bridge to the practical world of fuel cell development along a path where irreversibilities are recognised for what they are – undesirable concessions in which potentially useful work is given up. The crux of Mr Barclay’s book is his revision of the nature of isothermal oxidation, the process which generates the potential difference of
a fuel cell, at zero-current equilibrium, or when generating current and power. Mr Barclay places the maximum possible work of a fuel cell at a very high new level, and dismisses the calorific value of the fuel as a basis of comparison for fuel cells. The revision is far reaching, and will undoubtedly be accepted only slowly and begrudgingly by a field that is quick to open up fresh searches for paradigm shifts but is slow to recognise brilliant fresh thinking in its midst.

The book is doubly ambitious in attempting to point the way to the ‘hydrogen mine’ or source of low-cost hydrogen. Moreover it highlights the difference between compressible gaseous fuels and relatively incompressible liquid fuels for fuel cells.

Mulling over of the book will be an extended task for fuel cell and hydrogen economy protagonists, and we must await the results. Perhaps a piece of common ground is to look forward to economical coal utilisation via distillation of gaseous fuel for integrated fuel cells and gas turbine engines. Or then again perhaps, armed with fresh thermodynamic insight, there are better ideas to be had on how to use nuclear power to extend the work obtainable from gas and oil.

Gerry Agnew
Vice-President, Rolls-Royce Fuel Cells
Derby, UK
Introduction, and
Commentary on Matters
Affecting all Chapters

A child’s amang ye, takkin notes!
And, faith, he’ll prent it.
Robert Burns

This introduction is rather long, since it includes that matter which is common to all of the following chapters in the book, some of which are new and unique to the book. A first-time lead is provided into the revolutionary new technology of isothermal oxidation, detailed in the thermodynamic appendix (Appendix A). The reaction in a fuel cell is isothermal, charge exchange, oxidation. Combustion does not occur, and its theory does not relate to fuel cells, nor does its main parameter the calorific value or combustion enthalpy.

The author’s position is roughly that implied in Burns’ remark above. The fuel cell community is young and interdisciplinary. Retired fuel cell technologists are still rarities, so that distillations of long-term extensive experience are hard to come by. Moreover, such experience will not have been against the new background fully developed in this book for the first time. The new fuel cell isothermal oxidation theory is remarked upon in the foreword, and was partly introduced by Barclay.
It is a noteworthy worldwide failure that isothermal oxidation is not the industry-recognised modus operandi of the fuel cell, although it is without doubt that it should be, and must be in the future, in the author’s view.

It is the function of this book to correct this time-hardened situation, and to refocus the priorities of the development problems of the worldwide industry, from fuel cell makers to hydrogen manufacturers. The confusion is such that the fuel cell should be redefined. It is not enough to refer to continuously fed fuel and oxidant electrodes. The interfacial chemical reaction via isothermal charge interchange at the electrolyte–electrode interface is the other essential feature. The fuel is oxidised (electron removal) and the oxidant reduced (electron addition). Any supposed resemblance between reversible isothermal oxidation and irreversible combustion should go into the rubbish bin of history.

A hydrogen–oxygen gaseous fuel cell, and the regenerative *incompressible liquid-fuelled* redox flow battery of Chapter 2, share isothermal oxidation as their modus operandi. The redox flow battery cannot be classified as anything other than an alternative kind of fuel cell. Denying that the redox flow battery is a fuel cell is equivalent to King Canute’s battle with the tide. See the latter part of point 10 below for additional remarks on the definition of the fuel cell’s modus operandi.

1. *Isothermal chemistry in nature.* Nature in its vegetation and its animal life uses isothermal chemistry to achieve high efficiency. The fuel cell is the first human device to follow nature. The industry, however, has largely failed to see it that way.

Whereas an aeroplane has a Carnot limited engine with a hot exhaust, the familiar, but contrasting, example of the swan is a significant flying machine propelled by isothermal muscle power, rather than an engine. The cells of living creatures are packed with small chemical plants, termed mitochondria. These, nourished by blood, have the task of providing the exact materials to enable the creature to be self-maintaining, and of manufacturing the fuel for contractile muscles. This fuel is named adenosine tri-phosphate, which hydrates to adenosine di-phosphate when used, and is reprocessed to tri-phosphate in the mitochondria. The complex, liquid reagent, isothermal, chemical process of the mitochondria is known as the Krebs cycle (Campbell *et al.*, 2006) but the reversible entropy changes of its near equilibrium thermodynamics are not yet tied down. The swan, however, does give us a prima facie indication of very high efficiency. Swimming on a
pond, the swan takes in small animals, bugs and vegetation. From that apparently meagre fuel it can produce the substantial power needed to take off into flight. No combustion engine fired with the latter fuel could achieve such a performance.

Twenty-five years ago in Madras (now Chennai), India, the author witnessed the excavation and spoil removal, for the foundations of a nuclear power plant, by a numerous team of women in scarlet saris. They had bid for and won the contract against bulldozers, a triumph for low-cost, efficient, rice-fuelled muscle power. With the graceful deportment born of their traditional task of head-high water carrying, they moved spoil in shallow circular trays on their heads. They walked up out of the foundation pit in an organised spiral, effectively an inclined plane. The reader should recognise that rice from photosynthesis is the product of another isothermal chemical reaction which absorbs the sun’s power, without raising the temperature of delicate greenery. We, who are muscle powered, are therefore also solar powered.

In ancient cases like the construction of the Egyptian pyramids, muscle power did not have a competing mechanical alternative.

The oft quoted example of the isothermal photosynthesis reaction is fructose production. Carbon dioxide and water are forced together, by solar power, catalysed by chlorophyll. Oxygen is released. That is,

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

2. *Isothermal chemistry in fuel cells.* Barclay (2002) wrote a paper which is seminal to this book, and may be downloaded from the author’s listed web site. The text and calculations of this paper are reiterated, and paraphrased, extensively in this introduction. Its equations are used in Appendix A. The paper, via an equilibrium diagram, draws attention to isothermal oxidation. The single equilibrium diagram brings out the fact that a fuel cell and an electrolyser which are the thermodynamic inverse of each other need, relative to existing devices, additional components (concentration cells and semi-permeable membranes), so as to operate at reversible equilibrium, and avoid irreversible diffusion as a gas transport mechanism. The equilibrium fuel cell then turns out to be much more efficient than a normal fuel cell. It has a greatly increased Nernst potential difference. In addition the basis of calculation of efficiency obviously cannot be the calorific value of the
fuel, since irreversible burning is not involved. The correct basis is asserted to be the fuel chemical exergy, as defined by, and calculated using, the equilibrium diagram of Barclay (2002) and in Appendix A of this book, Sections A.2.16 and A.2.17.

3. *Engine efficiency.* There is also the buried and forgotten fact that engine efficiencies as usually calculated enable one engine to be compared with another, but are gross overestimates of absolute or exergetic efficiency. The comparison of fuel cell with engine is greatly affected. This subject is enlarged upon in point 17 below, on combustion irreversibility,

4. *Multidisciplinary fuel cells.* In the fuel cell engine and hydrogen business, communication between the disciplines of equilibrium and irreversible thermodynamics, physical chemistry, electrochemistry, fluid mechanics, materials science and mechanical arrangement, to name but a few, is visibly open to improvement.

This book, as commissioned the now inactive Professional Engineering Publishing (PEP), was intended merely to be an expansion of the chapter on fuel cells in the author’s PEP book on exergy analysis (Barclay, 1998), pp 69–89, and hence to be a review of the status of the competing fuel cell types. However, during the Seventh Grove Symposium, the author grasped the undoubted fact that the chemical reaction in all fuel cells is not combustion, but isothermal oxidation, and as a result wrote his 2002 paper. This was clearly incompatible with the fact of isothermal oxidation, which produces power directly without the kind of energy conversion occurring in heat engines, to characterise any fuel cell in terms of the calorific value of its fuel, in joules. But that is what the worldwide fuel cell industry was doing, and still is doing. It was, and is, a case of not understanding Joule’s experiment, Figure 3.1.

Incidentally, the author’s activities paused after publishing his 2002 paper, while an early version of this book was completed for PEP. Recently, in 2005, the author went through the index of the *Journal of Power Sources* from Vol. 151 in 2005 and back to the Eighth Grove Symposium, Vol. 118, 2003, so as to modernise the text.

A prime lesson in irreversible process theory is based on Figure 3.1. In that experiment, shaft power was dissipated irreversibly by a rotating paddle, to become energy in a tank of near
ambient temperature water. The chaotically interactive translation, vibration and rotation of the water molecules is energy:

\[ 1 \text{ Ws} \gg \text{irrev} \gg 1 \text{ J} \]

or

1 J at ambient temperature cannot be reconverted to 1 Ws.

Energy is accessible to generate power only by cyclic processes (heat cycles) as defined by Carnot. (Carnot cycle theory is outlined below.) Energy conversion, as in heat cycles, is not encountered in fuel cells. Fuel cells generate electrical potential difference directly (Barclay, 2002) from the chemical exergy or Gibb’s potential of their fuel. Potential difference is an amount of work. Hence fuel cells are not Carnot limited. Practical fuel cells suffer from many losses or modes of exergy annihilation, or irreversibilities, as exemplified in Figure 3.1. Those modes are the subject of Chapter 3.

A brief digression is that in Einstein’s famous equation

\[ E = Mc^2 \]

the symbol \( E \) is in fact for exergy, and not for Carnot limited energy. Einstein also overlooked Joule’s experiment.

There are two incompatible sayings in present-day thermodynamic usage. These are, firstly, that the entropy is always on the increase (true); and secondly, that energy can neither be created nor destroyed (false, but rather popular). The former asserts that there is a continuous supply of energy, and the latter, based on \( 1 \text{ Ws} = 1 \text{ J} \), rather than \( 1 \text{ Ws} \gg \text{irrev} \gg 1 \text{ J} \), denies the existence of such an energy supply. Energy creation occurs in Figure 3.1.

Gerry Agnew of Rolls-Royce predicts in his foreword to this book that grudging admission of this efficiency difficulty may take an extended period. The author is impatient to improve on that prediction, and presented his work (Barclay, 2002) at an IMechE conference on 30 November 2005 in pursuit of that objective. The conference chairman accepted that the calorific value was no longer a valid performance criterion. In a discussion, the author presented an extensive calculation of the power yield of isothermal oxidation, relative to the yield of combustion allied to a heat cycle.

The correct fuel cell characterisation (Barclay, 2002), it is reiterated, is via the ‘fuel chemical exergy’ in watt seconds, and numerically a much larger quantity than the calorific value in joules. Fuel
chemical exergies are derived numerically for varied cell operating pressures and temperatures, in Appendix A, along the lines initiated in Barclay (2002). Notional isothermal reactant and product circulators (concentration cells) are used in lieu of the irreversible diffusion which moves the gases in real fuel cells. The **greatly enlarged development potential of the complete fuel cell with circulators** is pro rata to the large fuel chemical exergy

$$\Delta G = H - b - T(S - s)$$

which, like electrical potential difference, is an amount of work done. Numerically, as calculated in work units, W s, from the equilibrium diagram, Figure A.1, the fuel chemical exergy, $\xi_{\text{ch}}$, is about 2.0 times higher than the calorific value in energy units J (which needs to be multiplied by the cycle efficiency, say 50%, to reach the value of the cyclic output). Note that the existing literature, the actual editions used by the author, including Kotas (1995) and Moran and Shapiro (1993), does not use equilibrium concentrations for fuel chemical exergy calculation (Chase et al., 1985), in the fuel cell chemical reaction, and puts $\xi_{\text{ch}}$ numerically equal to the net calorific value. The hydrogen fuel cell (Figures A.1 and A.2), aided by three concentration cells for the isothermal expansion of hydrogen, oxygen and steam, is a fourfold potent device, when correctly calculated, compared with an assessment via combustion theory.

5. *This book versus alternative textbooks.* Four book titles follow, which do not follow the line of Barclay (2002). In any discussion of isothermal oxidation at the fuel cell electrolyte–electrode interface the four example books suffer from a lack of thermodynamic rigour.

(a) Vielstich *et al.* (2003). This is a large fuel cell compendium with much useful detail but based on irrational combustion theory for performance calculations.

(b) Hoogers, *et al.* (2002). This book recognises the part played by the change in Gibb's potential but not the significance of chemical equilibrium (Chase *et al.*, 1986), and therefore of concentration cells as circulators.

(c) Linden and Reddy (2002). This book uses irrational combustion theory.

(d) Larminie and Dicks (2000). This book uses irrational combustion theory.
There are two other well-known books which also should be commented on:

(a) Kotas (1995). In this book, Figure 2.12 is used to prove that the fuel chemical exergy and the lower calorific value of the fuel, with different units, are numerically equal. The conclusion does not appreciate the need (Atkins, 1995) for the reactants and their product in the van’t Hoff equilibrium box to have equilibrium concentrations (dissociation concentrations). The reader must be aware that this affects the whole book and many calculations.

(b) Moran and Shapiro (1993). Figure 13.3 of this book takes no account of the need for equilibrium concentrations in fuel cell reactions. Figure 13.4 also needs a reversible reformer to feed H\textsubscript{2} and CO to separate fuel cells.

This book, however, seeks to correct the apparent 150-year-old distorted perspective of the industry, highlighted by the incompatibilities between, and contradictions amongst, the texts above and the author’s published paper (Barclay, 2002).

Sir William Grove’s interpretations of 150 years ago, that his fuel cell notion was the inverse of his electrolyser notion, need to be updated before relatively efficient complete fuel cells, integrated with comparatively low-performing gas turbines, are developed and can reach the market (Figure A.7). The integration serves the purpose of burning in gas turbine combustion chambers fuel which the isothermal oxidation reaction is unable to consume. In the practical system, the result is superior starting (preheating) capability, by driving the gas turbine compressor from the power grid. Irreversible burning, in a combustion chamber, is unfortunately the only option, but an inefficient one to isothermal oxidation in the fuel cell.

It is again asserted that the numerical basis of efficiency in fuel cells, engines and combinations thereof is the fuel chemical exergy, derived from Figure A.1. The resulting unwelcome and tedious problem must be faced of changing mind sets, and a mass of efficiency figures, in the downwards direction. The good news is that the development potential of the fuel cell is bigger pro rata than the large fuel chemical exergy, with the proviso that new perm-selective membranes and concentration cell circulators need to be developed, before the superior potential can be realised.