Thermodynamics Background and the Properties of Water

3

This chapter has the aim of explaining the thermodynamic principles and calculation processes used in the remainder of the book. Parameter definitions and the first law of thermodynamics are introduced, followed by the Steady Flow Energy Equation, from which the definition of specific enthalpy emerges. Entropy and absolute temperature are introduced next, based on an explanation of Carnot's work. The thermodynamic and transport properties of water are described, focusing mainly on properties along the saturation line, in particular, formulations produced by the International Association for the Properties of Water and Steam (IAPWS). The chapter ends by examining hydrostatic pressure and the boiling point for depth curve.

3.1 Definitions and the First Law of Thermodynamics

Engineering thermodynamics tends to focus on the conversion of heat to work, a process which was a mystery when heat was regarded as some sort of fluid contained in limited amounts within a substance. Rumford found that boring bronze cannon with a blunt drill appeared to release an unlimited amount of the "fluid", and his observations were a key step in understanding that heat and mechanical work are equivalent. Today the idea that energy comes in a variety of interchangeable forms is commonplace; however, thermodynamic reasoning depends on the use of precisely defined terms which must first be introduced.

The changes that take place in a substance when it exchanges heat and work with its surroundings are the focus of thermodynamics. Some authors (e.g. Pippard [1961]) distinguish between classical and phenomenological thermodynamics, the latter drawing on physical observations such as the molecular properties of a substance in any reasoning, whereas the former depends on the bare thermodynamic laws and postulates only, without reference to the wider physics. No such distinction is required here, and simple molecular models will be appealed to sometimes.

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Neither heat nor work has any material form, but both are quantifiable in terms of the effect they have on materials. The logical way to approach any quantitative analysis of the effects of exchanges of heat and mass with some amount of a material is to first define the latter; traditionally, this is referred to as "the system". The system is chosen to suit the analysis to be carried out. All of the analyses in thermodynamics and thermo-fluids are based on conservation rules. If the focus of attention is what is happening within the cylinder of a steam engine, as it usually was in the early days of engineering thermodynamic development, then the system is defined as the mass of fluid contained by the cylinder and its piston. For the study of fluid inclusions in crystals, the system might be the inclusion itself. If heat and/or work cross the boundary in either direction, a change in the system takes place, recognisable by changes in certain physical parameters.

Historically, the focus was on a closed system containing a given mass of substance (typically a gas such as air or steam) which did not cross the boundaries, although heat and work did. More precisely, the simplest system is a fixed mass of a single-component homogenous fluid which is not undergoing any chemical reaction, contained within a clearly defined boundary. A full gas cylinder with the valve closed matches this description, as does the cylinder of an internal combustion engine with the valves closed but with a moveable piston. In both cases the substance and the system boundaries are defined, and heat exchange to or from the substance must cross the system boundaries. Work exchange with the fluid in the cylinder is possible by means of the moving piston, work being defined as force times distance moved, but it is not possible for a closed gas cylinder to produce any work output by itself.

The state of the substance filling the system can be defined by two parameters, its pressure P and its temperature T. The energy content of the substance is defined as U, the specific internal energy in units of kJ/kg (specific means per unit mass); substances may have additional energy in other forms, but for a fixed mass contained within simple boundaries and with no chemical reaction taking place and no movement (kinetic energy) or gravitation (potential energy), U defines the energy content. If the system has only recently exchanged heat or work, there may be internal temperature gradients and internal motion. When these have died away and the system can be said to be in equilibrium, P and T are sufficient to define U for the given substance. It follows that if U and P are known for a particular case, then T is at least fixed, even if its value has not been measured. For any given case, the state of the system is known if two of these three parameters are known, and it should now be clear that "state" refers to the energy level of the system. There are parameters other than U which together with P or T define the state of the system. They are related to U and are referred to in engineering thermodynamics as "functions of state".

To make a further step towards analysis, temperature and pressure must be defined. Fahrenheit invented the mercury-in-glass thermometer and his temperature scale in the early eighteenth century. Celsius introduced his scale in the same period, his scale being sometimes called "Celsius", but sometimes "Centigrade" because he divided it into 100 units. Both inventors used different scales and datum points, which are still well known. Mercury-in-glass thermometers, thermal

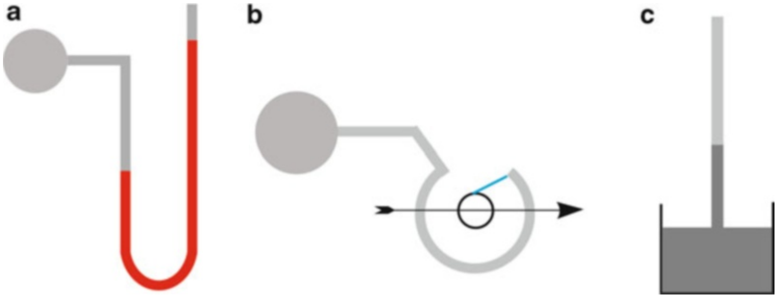


Fig. 3.1 (**a**) A simple manometer and (**b**) a Bourdon pressure gauge, both measuring the pressure in a pipe, and (**c**) a barometer

expansion in solids, change of electrical resistance with temperature and the generation of a voltage between dissimilar metals have all formed the basis of temperature measuring instruments. A loss or gain of heat is usually associated with a temperature change, although an exception discussed later occurs when phase change takes place.

Pressure is defined as the force per unit area exerted by a substance on the walls of its container. If the substance is a solid it requires no container. If its shape is such that one part of its boundary surface is flat so that the solid can stand on a flat plane, then gravity exerts a force that gives the substance weight, and the weight exerts a pressure on the flat plane. Very often the substances requiring thermodynamic analysis are fluids. A fluid may be defined as a substance with no shape of its own—it takes up the shape of its container. No further adjustments to this definition are needed if the fluid is a gas and the system has closed boundaries, such as a gas cylinder. The molecules of the substance fill the container, they have kinetic energy and exert a pressure on the container walls by colliding with it, and the pressure has the units of force/unit area (kgm/s^2 per m^2 or Pa). The classic engineering thermodynamic study is of a gas filling a cylindrical vessel with one end closed and the other formed by a piston capable of axial movement. The pressure of the gas, P, exerts a force F on the piston, which presents an area A to the gas. The magnitude of the force is $F = P.A$ in units of kgm/s^2 which are equivalent to Newtons (N). If the piston is allowed to move an axial distance dx, then the work done by the gas on the piston is $P.A.dx$, or $P.dV$, where dV (m^3) is the increment of volume over which the piston moves. The movement of the piston must be at right angles to the force for this expression to hold. In general the pressure exerted by a gas on its container is normal to the surface, so a similar approach to calculating the exchange of work involved would be applicable to the expansion of a balloon with a flexible envelope and many other situations.

If the fluid is a liquid, its definition differs from that of a gas, because a liquid will always fall to the lowest level in a container which is in a gravitational field. The surface of the liquid at rest will be horizontal. The manometer is a means of pressure measurement which makes use of this phenomenon. The manometer, shown in Fig. 3.1a, automatically measures the pressure relative to atmospheric pressure. The same applies to the Bourdon tube, Fig. 3.1b, which remains a popular instrument and works because the exact shape of a curved tube with a difference in pressure between inside and outside depends on the magnitude of the pressure difference. When the pressure difference changes, the end of the tube changes position; it is attached to a drum by a fine wire, and the drum and pointer rotate accordingly—the drum is spring loaded. It is because the Bourdon tube measures the pressure relative to atmosphere that the term “gauge pressure” was introduced; atmospheric pressure must be added to gauge pressure to obtain absolute pressure. Absolute pressure is used throughout this book and is recommended always. Quartz crystal piezometers are available for electronic recording of pressure; compression of the crystal generates a voltage. Atmospheric pressure is measured using some form of barometer, of which that shown in Fig. 3.1c is perhaps the simplest; it is used on a large scale in creating vacuum in some types of power station condenser (see Fig. 11.16).

Heat is a form of energy and if two systems at different temperatures are placed in contact, heat will flow from the one with the highest temperature into the other. Energy flow is recognisable by the existence of a temperature gradient. This being so, then temperature gradients must occur within a system sometimes rather than just across contacting surfaces—the heat arriving from another system in contact with it establishes a higher temperature in the region where it arrives, which enables its transfer to the rest of the system. In solids, it can be imagined that the molecules vibrate but stay in fixed positions, whereas in fluids they are free to move about. In solids the amplitude of the vibration can be imagined to be directly proportional to temperature, so the condition of thermal equilibrium, at which temperature is everywhere the same, is one of mechanical equilibrium in which all the molecules vibrate to an identical extent. Heat is transferred in solids only by this process, which is known as thermal conduction. Heat transfer by thermal conduction also takes place in fluids but usually accompanied by other transfer processes. Because the molecules of a fluid are free to move, a collection of molecules at a high temperature can migrate as a whole to another part of the system where the fluid is colder, where they share their heat with their new neighbours. This is the process that takes place when fluid is stirred, a highly effective way of producing homogenous and isothermal conditions. Thermal conduction, defined as heat transfer without movement, still takes place in moving fluids but it is no longer the dominant mode of heat transfer. For it to be the only mode of heat transfer in a fluid filled system, the system must be specially designed to prevent fluid movement, as in the case of domestic double glazing, for example. Heat transfer in fluids in the general case where movement takes place is called thermal convection. Earth scientists sometimes use the term “advection” as a general description of transfer of heat and/or mass, but the term is not used by engineers—it has no clear, generally accepted meaning.

The transfer of heat across the boundary of a system containing a single-phase substance is detectable by the measurement of temperature difference; the temperature of a block of metal rises if it is exposed to a flame. The increase in energy level of the system can be quantified by the rise in temperature once equilibrium has been achieved, but not the absolute energy level if the only temperature scales available are Fahrenheit or Celsius, which are arbitrary scales; the "absolute scale of temperature" resolves that issue, Sect. 3.3 below.

Based on the above definitions and general discussion, it is possible to summarise as follows. The state of a substance is in general terms a measure of its energy content and is quantifiable as $U(P,T)$ and by other functions of state yet to be introduced. Energy is interchangeable between its different forms and is interchangeable with work; it is conserved, that is, it cannot simply disappear or be "consumed"—the equivalence of mass and energy via nuclear reactions is not considered here, and mass also is regarded as being conserved. All of these statements are combined as an energy conservation equation:

$$dQ - dW = dU \tag{3.1}$$

which is known as the first law of thermodynamics. In this equation only U is a function of state, and the equation states that the net effect of dQ and dW, which are merely additions or subtractions of energy, is to change the state of the substance in the system. Some people replace dQ and dW in the equation by δQ and δW, respectively, as a reminder that Q and W are not functions of state, because many thermodynamic calculations rely on a set of differential relationships between the functions of state (Maxwell's equations—see e.g. Perrot [1998]). The absolute level of specific internal energy does not appear in the equation, only the change in level, dU. The algebraic signs of the heat and work terms are traditional for engineering use because the first major application of thermodynamics was to "heat engines", prime movers which converted the heat of combustion into work. Heat was always added to the system and work always left it (at least, that was the intention!). Thus, heat added to the system is positive and work done which leaves the system (i.e. work done by the system) is also positive.

Finally, it is essential to note that all of the above explanations have been built on the idea of a closed system—the cylinder with a piston in which a fixed mass of substance was locked up. The mathematics for this circumstance are the simplest, but there is no objection to allowing mass to enter and leave the system—the rules of continuity of mass simply have to be adhered to within the new boundary conditions. This is a more general case and vital for the present purposes, to analyse the natural and induced flows in resources and the flows in surface equipment and power stations. Calculation processes must be set up to deal with a continuous flow of geothermal fluid to generate power, which is defined as a rate of production of work.

3.2 The Steady Flow Energy Equation and the Definition of Specific Enthalpy

Many of the major engineered flows needing thermodynamic analysis are steady-state flows, invariant in time, and the Steady Flow Energy Equation (SFEE) is a common topic to be found in many thermodynamics texts. A power station

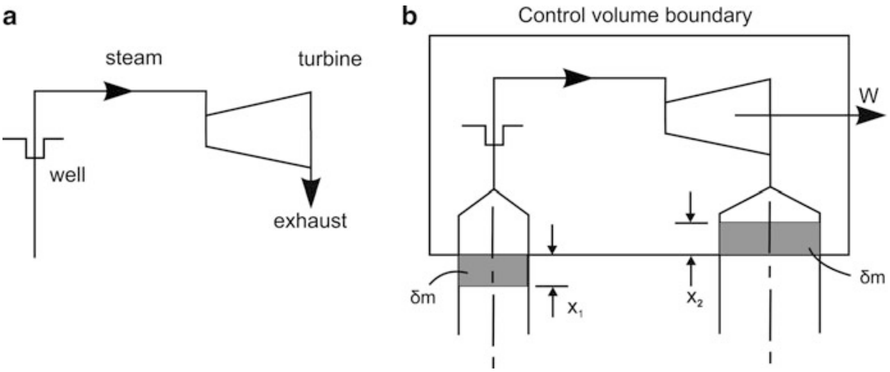


Fig. 3.2 (**a**) Diagram of a system comprising a well and turbine and (**b**) its representation as a control volume with work and increments of flow in the well and turbine exhaust (*shaded*) crossing the boundary

operating at a steady output is an example. A more general form of the energy equation incorporating transients is necessary to analyse unsteady conditions and also sometimes appears in reservoir engineering analyses. The SFEE is a restricted form of the general time-dependent equation, so the logical order would be to produce the general form first and then reduce it to the SFEE. However, the SFEE provides an easy introduction to specific enthalpy and the explanation of throttling (adiabatic pressure reduction) so will be examined first. Fluid density now needs to be introduced. It is defined as ρ (kg/m^3), the mass per unit volume of the substance, but it appears just as often in its inverse form, specific volume V (m^3/kg), where $V = 1/\rho$. Specific volume is a function of state, that is, it is determined if two of P,T, U or any of the other functions of state yet to be introduced are known.

3.2.1 The Steady Flow Energy Equation

The diagrammatic arrangement of a well supplying steam to a turbine is shown in Fig. 3.2a, and it is shown at a more suitable level of detail for the present purpose in Fig. 3.2b. What is to be developed is an equation, equivalent to Eq. (3.1), for a system with mass crossing its boundaries. The system boundary is defined, but it is a schematic boundary rather than an actual one. It is best referred to as a control volume, the space within which the relevant rules are to be applied.

The well in Fig. 3.2a discharges continuously and supplies a constant mass flow rate of steam to the turbine, which produces a steady work output and a steady flow of exhaust steam. Fluids are moving, but steadily, so there is no change of any variable with time at any point within the control volume. The general approach used in deriving the equation has been used by many authors, according to Rogers and Mayhew [1967]; a small mass of fluid, shown shaded in Fig. 3.2b, is followed as it enters the control volume from the well and a matching mass leaves in the turbine exhaust pipe. The small mass, δm, enters the control volume from the well.

It has specific internal energy U_1 and energy in the form of kinetic energy, $\frac{1}{2}\rho_1 u_1^2$, and potential energy gz_1 relative to some datum elevation $z = 0$ which needs no further definition at present. It is pushed into the control volume in a time δt under a pressure difference, while an equal mass exits the control volume at the other end, with a different set of energy components, U_2, $\frac{1}{2}\rho_2 u_2^2$ and gz_2. The exact detail of the entering and leaving masses must be examined because work is involved. Suppose the control volume ends in the production casing of the well so that it exactly includes the shaded volume. The casing has an area of cross section A_1. The mass δm_1 occupies a length of casing x_1 and its volume $A_1 x_1$ may also be written as $\delta m_1/\rho_1$. The work done on the control volume, which is negative according to the sign convention, is

$$\delta W_1 = P_1.A_1.x_1 = \frac{P_1}{\rho_1}.\delta m \tag{3.2}$$

At the exit, the same form of expression for δW is obtained:

$$\delta W_2 = P_2.A_2.x_2 = \frac{P_2}{\rho_2}.\delta m \tag{3.3}$$

but the work is now done by the system, pushing the mass δm out so it is positive. Work is also done by the system on the turbine, which appears as W and is also positive. The first law, Eq. (3.1), is now considered and the work and energy terms are introduced. The energy within the control volume as a whole, excluding the δm increments, is referred to simply as E. It is an important part of the concept that although the fluid is moving through the system and changing as it goes, at any point within the control volume all the variables describing the system are constant with time, so E does not change with time.

Thus, the form of Eq. (3.1):

$$dQ - dW = dU$$

can be adopted with the new terms so that

$$\left(dW + \delta m\left\{\frac{P_2}{\rho_2} - \frac{P_1}{\rho_1}\right\}\right) = \left(\delta m\left\{U_2 + \frac{u_2^2}{2} + gz_2\right\} - \delta m\left\{U_1 + \frac{u_1^2}{2} + gz_1\right\}\right) \tag{3.4}$$

The energy within the control volume, E, does not appear in the equation since it is unaffected—by definition the variables at any point in the control volume are invariant with time. No heat exchange has been built into the arrangement being represented (Fig. 3.2a), so there is no term equivalent to dQ. The signs of the heat and work exchange defined for Eq. (3.1) have been applied. There is continuous power output from the turbine, which draws attention to the fact that the units of power are J/s (Watts) and of work are J. The units of the equation are Joules.

Table 3.1 Examples of the properties of saturated water and steam at various temperatures

T_s (°C)	P_sV_f (kJ/kg)	h_f (kJ/kg)	P_sV_g (kJ/kg)	h_g (kJ/kg)
25.0	3.18	104.8	137.2	2546.5
175.0	1.0	741.2	193.3	2772.7
350.0	28.76	1670.9	145.48	2563.6

Reintroducing *dQ* to allow for heat exchange produces a more general equation, and replacing *1/ρ* by the specific volume *V* and reorganising the terms result in

$$\frac{dQ}{\delta m}-\frac{dW}{\delta m}=\left(U_2+P_2V_2+\frac{u_2^2}{2}+gz_2\right)-\left(U_1+P_1V_1+\frac{u_1^2}{2}+gz_1\right) \tag{3.5}$$

The terms on the right-hand side are all specific (per kg), and those on the left are also per kg. The rate of work output is per kg of mass flowing through the system, so the introduction of a mass flow rate in kg/s will enable the rate of power output and heat loss or gain to be calculated. Although the *PV* term has the same units as *PdV*, the latter is the work *dW* done by a force acting on an area and moving a distance, as a piston in a cylinder, for example. The *PV* term in Eq. (3.5) relates to the energy within a volume of fluid as a result of it being at a pressure *P*. A change in *PV* might produce work, given suitable arrangements, but not necessarily, so the term must not be thought of as a work term.

3.2.2 Specific Enthalpy

Because *U*, *P*, and *V* are all functions of state, then so is the combined term $U + PV$, which is known generally as enthalpy, and in this equation is specific enthalpy (kJ/kg). It is customary to write the Steady Flow Energy Equation as

$$Q-W=(h_2-h_1)+\frac{1}{2}\left(u_2^2-u_1^2\right)+g(z_2-z_1) \tag{3.6}$$

where *Q* and *W* are now heat and work transfers per unit of mass flow (J/kg).

It is useful to know the order of magnitude of the terms in this equation and in the definition of *h*.

The saturation conditions for water are given in Table 3.1 for three values of T_s to cover the range of interest here, together with *h* and its components.

The first thing to notice in Table 3.1 is that the entries do not all increase with temperature. There is a maximum in the specific enthalpy of saturated steam at approximately 235 °C which has been speculated to be the cause of some phenomena observed in geothermal resources but which is not important for this discussion of the relative magnitude of *PV* as a fraction of *h*. For saturated water the P_sV_f term is 3 % or less of the specific enthalpy of saturated water—in other words the specific internal energy accounts for 97 % of the specific enthalpy. For saturated steam the P_sV_g term is 7 % or less of the specific enthalpy of saturated steam—the specific internal energy accounts for 93 % of the specific enthalpy.

3.2.3 The Kinetic and Potential Energy Terms in the SFEE

The order of magnitude of the terms in the SFEE should be examined for relative importance for each application. Taking the potential energy terms first, most engineering plant has a height of a few tens of metres. Taking 50 m as an example, the g_z term from top to bottom of the plant is 490.5 J/kg. Although the energy terms in Table 3.1 are in units of kJ/kg, Eq. (3.6) is in J/kg. Over 50 m then, the potential energy change is a mere 0.5 % of the smallest value of h_f in the table. However, geothermal wells are in a different league. For a well producing at a temperature of 350 °C from a depth of 4,000 m, the specific enthalpy at the wellhead would be 39 kJ/kg less than at the production zone. This is no doubt a small loss of energy in power station terms, but it is large enough to be accounted for.

The design velocity in water pipelines is usually of the order of 3 m/s, at which the kinetic energy term $u^2/2$ has a value of 0.0045 kJ/kg—a negligible energy consideration. The exit velocity of steam from a condensing steam turbine however can equate to a kinetic energy of 20 kJ/kg, and in large turbines the loss is enough to attract attention to the design to the exhaust ducting. The sonic velocity in steam, of order 425 m/s, provides a value of $u^2/2 = 91$ kJ/kg, or 3.6 % of the lowest tabulated h_g in Table 3.1.

3.2.4 Adiabatic Pressure Drop or Throttling

Sometimes steam is supplied through a pipe at a higher pressure than required—without a control valve, the flow through whatever is downstream would be too great. The control valve provides a local flow restriction. No work is done by the flow (there is no moving part to exert a force on anything and allow work to be performed) and the surface area of the valve is so small that the heat loss is negligible, even if the valve is uninsulated. There is no change of elevation. The SFEE, Eq. (3.6), thus reduces to

$$0 = (h_2 - h_1) + \frac{1}{2}\left(u_2^2 - u_1^2\right) \tag{3.7}$$

or if the kinetic energy terms are neglected,

$$h_2 = h_1 \tag{3.8}$$

The flow is said to be throttled, so throttling is thus a process in which there is little or no loss of energy. What is lost, however, is the opportunity to convert heat to work, so throttling of a flow from which electricity is to be produced must be avoided if possible. This is the next issue to be addressed in this chapter.

As a closing remark, the examination of the order of magnitude of the terms in the SFEE provides a clear message to those attempting to avoid global warming by using only mechanical energy such as wind power. The message is "thermal energy rules", which is why so much fossil fuel has been burned in the last 300 years.

3.3 Entropy and Absolute Temperature

There have been many different presentations of Carnot's work of 1824, e.g. Dugdale [1966] and Spielberg and Anderson [1987]. His ideas and the Carnot cycle remain difficult topics, but they must be understood if the concepts of entropy and absolute temperature are to be introduced.

Carnot set out to analyse heat engines, a new device at the time. To begin with it is sufficient to encapsulate his ideas in the comparison of heat flow with the flow of water downhill. The water flow can be interrupted with a machine and energy in the form of mechanical work can be extracted—it is not a necessity but an opportunity. The water continues to flow downhill after leaving the machine and would do so whether the machine was there or not. Likewise, heat flows from a high temperature to a lower one; it can be intercepted with a heat engine, a machine designed to convert heat into mechanical work, but it will flow regardless of whether the opportunity to convert some of it to work is taken or not. The classic diagram is shown as Fig. 3.3, in which heat flows from a source at temperature Θ_1 to a sink at temperature Θ_2 and is intercepted by a heat engine.

The new choice of symbol Θ for temperature is deliberate—T is reserved for °C, but Carnot's ideas require a less arbitrary definition of temperature which appears later in the discussion. Carnot thought of the heat engine from a practical point of view to the extent that he imagined a frictionless cylinder-and-piston reciprocating machine, containing a fixed mass of fluid. Any reduction in temperature of the heat, which can only flow from the higher temperature source to the lower-temperature

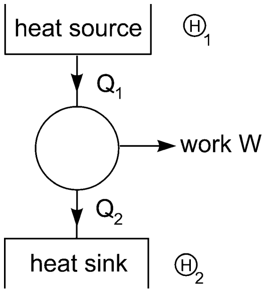


Fig. 3.3 Representation of a heat source supplying an engine which does work and rejects heat to a heat sink

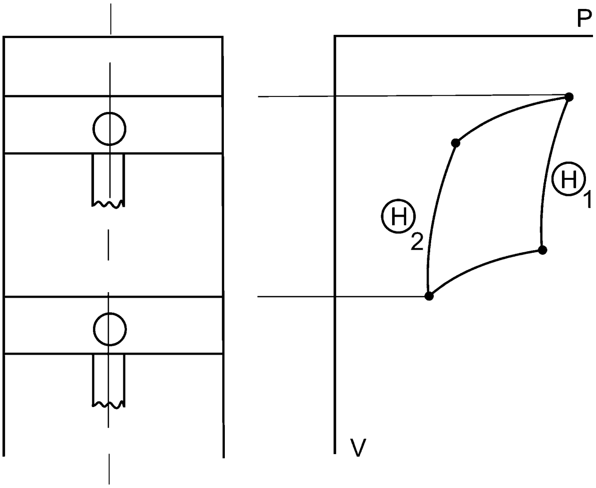


Fig. 3.4 A reciprocating engine following Carnot's cycle

source, he considered would be wasted unless it produced work as it went. Figure 3.4 shows the piston and cylinder, the axis of which lies parallel to the volume axis on the graph of volume against pressure of the working fluid mass, which he considered to be air—a helpful choice because anyone who has blown up a bicycle tyre knows that its temperature rises when it is compressed and can therefore be expected to fall if it expands.

The piston starts at the bottom of its stroke and as it rises the air is exposed to the low-temperature sink which keeps it at temperature Θ_2; how it is exposed is left to the imagination, perhaps the sink is portable and held up against the end of the cylinder. Heat must flow from the air to the sink as the air is being compressed. At some defined point, contact with the heat sink is removed, the cylinder is perfectly thermally insulated, and the air is compressed so that its temperature rises to Θ_1—it is not necessary to examine how the insulation can be applied or how the time to apply it could be decided upon. The piston has now reached the top of its stroke, at which time the air is exposed to the heat source at temperature Θ_1—the same temperature as the air. However, as the piston moves down and the air expands, the reduction in temperature that would normally take place is avoided by the presence of the heat source, which supplies heat to keep the air temperature at Θ_1. At a predetermined position the heat source is removed, the cylinder is insulated, the piston continues to move down, and the air expands, its temperature falling to Θ_2 exactly at the bottom of the stroke, the starting point.

The physics problems with this heat engine are obvious. All of the heat that flows from the source to the sink cannot possibly do so without passing through intermediate temperatures—heat flow without temperature reduction is not possible, heat only flows down a temperature gradient and must reach all the molecules of the working fluid. Yet the perfect engine requires that all heat flow must produce work. For the air to change temperature without transferring any heat to or from the piston and cylinder, the latter must have no thermal capacity, which is also impossible.

Finally, there is the practical problem of exchanging source, sink, and thermal insulation partway through the cycle. However, Carnot established the idea of a perfect heat engine. The net work produced is the integral of PdV around the cycle, which exactly equals the net heat flow. More heat is supplied from the source than is converted to work, so some is discharged to the sink. If this engine was reversed, supplying the amount of work produced would result in all of the heat being returned to the source; the engine is reversible—it does not just turn backwards, but reverses the changes in heat content of the source and sink exactly back to their starting values. Reversibility has come to mean the idealised exchange of heat or work in whatever situation. The work produced can thus be identified as $Q_1 - Q_2$ in Fig. 3.3, and it is possible to define a thermal efficiency as

$$\eta_C = \frac{Q_1 - Q_2}{Q_1} = \frac{W}{Q_1} \tag{3.9}$$

where W is the work output. The thermal efficiency is the fraction or percentage of the heat supplied which is converted to work. The ability of the Carnot engine to convert heat to work depends on the temperatures of the source and sink, and it can be reasoned that the thermal efficiency can be expressed also as

$$\eta_C = \frac{\Theta_1 - \Theta_2}{\Theta_1} \tag{3.10}$$

The Fahrenheit and Celsius scales predated Carnot's work and were arbitrary, so bore no relation to the temperatures in this equation. Kelvin proposed a new temperature scale on the basis of Carnot's work. The units of the new "absolute" scale, named degrees Kelvin in his honour, were chosen to match the Celsius scale in the 0–100 °C range, which resulted in the absolute scale zero being a very low temperature of −273.15 °C. A temperature of 273.16 K became the triple point of water (the condition at which steam, ice, and liquid water can coexist). It follows from Eqs. (3.9) and (3.10) that

$$\frac{Q_1}{Q_2} = \frac{\Theta_1}{\Theta_2} \tag{3.11}$$

which can be rearranged as

$$\frac{Q_1}{\Theta_1} - \frac{Q_2}{\Theta_2} = 0 \tag{3.12}$$

This sets the scene for the introduction of the concept of entropy. An elegant set of proofs establishing that entropy is a function of state is given by Fermi [1936], [reprinted 1956], although there are many to choose from in thermodynamic texts. He first proves that in a cyclic change, as in Carnot's ideal engine, the integral around the cycle of all exchanges of heat is zero if they are carried out reversibly:

$$\oint \frac{dQ}{\Theta} = 0 \tag{3.13}$$

and more generally for all cycles, reversible or not,

$$\oint \frac{dQ}{\Theta} \leq 0 \tag{3.14}$$

He then observes that the quantity dQ/Θ varies around a cycle, and at two points labelled A and B (without needing to say where these are or how many stages the cycle has—Carnot's had only 4, as shown in Fig. 3.4), the integral

$$\int_A^B \frac{dQ}{\Theta}$$

has a value that is independent of how the fluid changed from A to B, provided that it did so reversibly. If the change was reversible, there would be no transients of temperature or motion, and the states would be equilibrium states. If the change took place in a series of stages similar to those in Carnot's engine, the order in which the additions or subtractions of heat and the performance of work does not affect the value of the integral. In this way he establishes that

$$ds = \frac{dQ}{\Theta} \tag{3.15}$$

where s is a function of state referred to as entropy. It is a specific property, with units of kJ/kgK. It has some important properties, most notably that for any change taking place in an isolated system, the final value of the entropy can never be less than the initial value—entropy remains constant in reversible changes but increases otherwise. This is what Eq. (3.12) shows. As a result of friction in a flow, heat is produced and the entropy increases. It is possible to decrease the entropy of a system only by performing work on it.

Carnot's principles are very relevant to geothermal engineering. High-grade heat can be released by burning fossil fuels. The question must be asked whether there is any benefit to be gained by using high-grade heat to produce power and materials to extract low-grade heat from geothermal resources, when only a small proportion of that low-grade heat can be converted to work (electricity). Low-grade heat is being produced in abundance by society, but it is distributed and often in very small amounts. Converting high-grade heat to power leaves some low-grade heat, and the lower the source temperature, the more heat is left in theory, and in practice even more heat is rejected. This issue is central to economic optimisation.

3.4 The Thermodynamic and Transport Properties of Water

3.4.1 Phase Change, Clapeyron's Equation and the Saturation Line

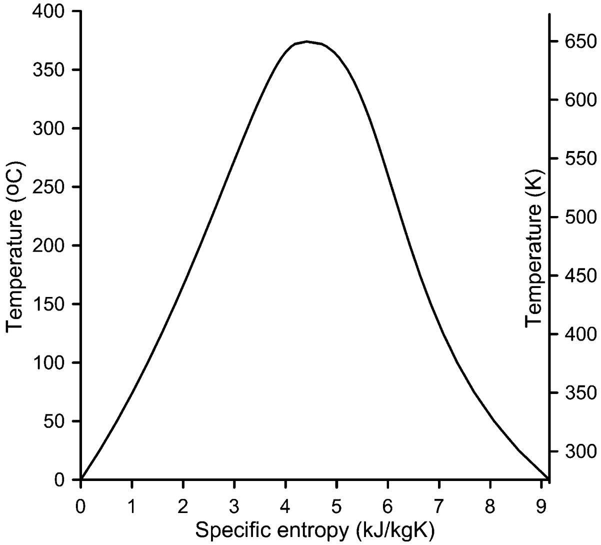
The important phase change here is that from liquid to gas. There is no fundamental distinction between gas and vapour. In the nineteenth century, it was observed that some gases could be condensed by compressing them only, whereas others had to be cooled as well, and this led to the two terms, vapour and gas. This difference in behaviour is due to the thermodynamic critical point parameters of the substance (P_c and T_c) relative to atmospheric conditions. The term vapour continues to be used by some authors to describe a gas when it is close to its saturation conditions. The flow of steam immediately downstream of the location of the boiling water producing it carries water droplets, due to heat loss and hence condensation. In this condition the steam may be referred to as "wet", and it is recognisable by its whiteness, which is not a property of the steam itself but a result of the water droplets internally reflecting light. Often a steam jet emerging from an orifice is totally transparent within a few centimetres of the exit, turning white downstream of that point. The transparent part is true steam, superheated, and free of the condensed water droplets in the white flow downstream; leaks of high-pressure steam in power stations are dangerous because they are invisible.

It is sometimes helpful to imagine liquid water with densely packed molecules ending at a surface above which the molecules are widely spaced and moving fast and randomly—they form a gas. The forces of intermolecular attraction at the surface are unbalanced, resulting in surface tension, which gradually decreases as P and T are increased towards the critical point. It can be imagined that the internal energy increases to saturation level at which the molecules disperse into their gaseous distribution, an idea useful in considering homogenous nucleation (see Chap. 7). Perrot [1998] explains that the saturation state is defined as the state at which the chemical potentials of liquid and gas are the same. Equilibrium points can be defined in terms of T and s, and the locus of points on the T–s diagram forms an envelope within (below) which the fluid is two phase and outside is either liquid or gas—Fig. 3.5.

There is no sharp distinction between liquid and gas except on or within the saturation envelope; put another way, fluid state can change from above the envelope on the left-hand side where it is liquid to above the envelope on the right-hand side where it is gas, without any surface between phases being observed. The envelope is the 1858 work of Clapeyron, who determined it as a P–V graph, since that was the age of reciprocating engines and reciprocating compressors for liquefying gases. He formulated an equation describing the saturation line as follows:

$$\left(\frac{dP}{dT}\right)_s = \frac{h_{fg}}{T_s.V_{fg}} \tag{3.16}$$

Fig. 3.5 Saturation envelope for water on *T–s* coordinates



It is not necessary to use the Clapeyron equation in this book, although it appears in connection with an equation in Chap. 7; it provided a means of defining the envelope and of actually measuring absolute temperature indirectly, by measuring fluid properties. The envelope can be plotted using steam tables. The essential point about the saturation line or condition for the present purposes is that P_s and T_s are a pair, so the three-parameter "rule" of functions of state reduces to two parameters at the saturation condition; it is only necessary to specify either P_s or T_s to fix all other functions of state at that value. In the form shown in Fig. 3.5, the saturation envelope is useful for plotting the thermodynamic changes taking place in a power station and comparing them with the ideal of reversible changes. The lowest pressure of practical interest here is condenser vacuum, so in Fig. 3.5 the temperature axis goes down only to the triple-point temperature.

3.4.2 Properties of Water

As the most common liquid on earth and the choice of working fluid from the earliest days of thermal power generation, it is at first sight surprising that the thermodynamic properties of water are still studied. The problem is that the precision with which the properties need to be known continues to increase, as well as the range of P and T over which they are needed, and their variation is complicated. For geothermal research the range extends from power station condenser pressures of 0.01 bars abs to ocean bed black smokers or deep subterranean aqueous solutions at thousands of bars abs and temperatures from 0 °C to well above critical (374 °C). For fossil-fuelled steam power engineering, very high precision is warranted because of the purity of the water used. The precision required is moderate

Table 3.2 A steamtable layout useful for geothermal engineering

P	T	h_f h_{fg} h_g	s_f s_{fg} s_g	ρ_f ρ_g	Cp_f Cp_g	λ_f λ_g	μ_f μ_g
Bars abs	°C	kJ/kg	kJ/kgK	kg/m^3	kJ/kgK	W/mK	kg/ms

for geothermal engineering because the fluids are not pure H_2O and the use of H_2O properties to describe geothermal water is already an approximation.

Traditionally, the thermodynamic properties required for power plant engineering calculations have been provided as "steam tables", in recognition that the variation of properties with P and T cannot be represented by simple formulae (their need predates hand calculators or computers other than the slide rule). Those steam tables focus on superheated steam. It is important that collaborating organisations use the same set of properties; otherwise a steam turbine manufacturer might contract to supply a turbine of a certain output when supplied with steam at specified rate and conditions, and the purchaser might wonder why his measurements suggested otherwise. Different sets of steam tables exist, with some significant differences in parameter values.

The International Association of the Properties of Water and Steam (IAPWS) [2012] updates the properties from time to time. Their publications are freely available for use. The needs for geothermal work differ from those for steam power engineering in general, because the main focus is on flashing and condensation processes, i.e. on saturation properties and rarely on superheat properties. A layout of property values which appears to be useful was produced by the author and Dr Sadiq Zarrouk for the University of Auckland Geothermal Institute based on the 1967 IFC formulation. The column headings and the units of the entries are shown in Table 3.2. The full table is in two parts, one with pressure in the first column, in regularly spaced increments, and the second with temperature in the first column.

In the specific enthalpy column, all three values are given: specific enthalpy of the saturated liquid, the difference between the specific enthalpies of saturated liquid and saturated steam and the specific enthalpy of saturated steam. The same applies to specific entropy. These help when calculating dryness fraction. Densities, specific heats, thermal conductivities, and viscosities are included although they are less often required.

A two-phase mixture can be defined in terms of its dryness fraction, X, which is the proportion by mass of the mixture which is steam; the proportion of water is $(1 - X)$. The specific properties, volume V, internal energy U, enthalpy h and entropy s, of the mixture are found by adding the saturated steam and water values in the appropriate proportions, thus for specific enthalpy,

$$h = (1 - X)h_f + Xh_g \tag{3.17}$$

This can be rearranged as

$$h = h_f + X(h_g - h_f) = h_f + Xh_{fg} \tag{3.18}$$

which is the reason for including h_{fg} in the tables.

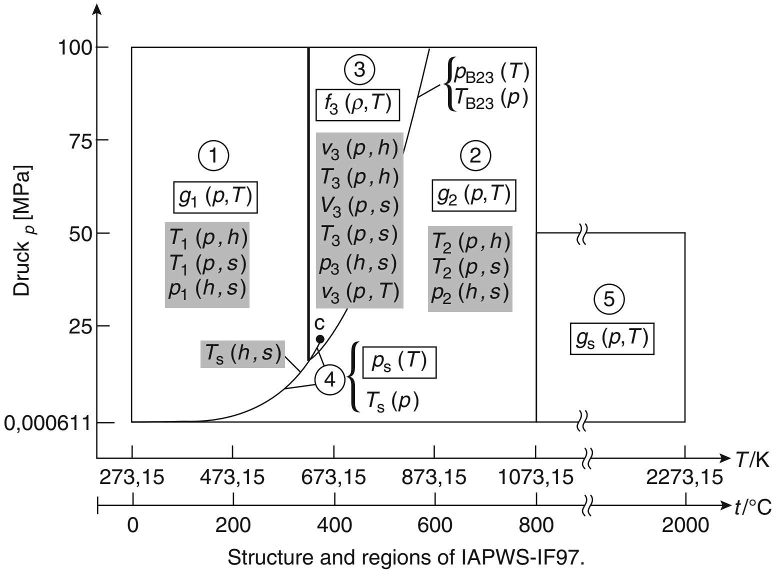


Fig. 3.6 Regions of the pressure–temperature plot into which the IF97 properties of water formulation are divided (Fig. 2.1 of Wagner and Kretzschmar [2008], published by Springer, second edition)

The mean density of the mixture must be found by following the additive rule above for specific volume:

$$V = (1 - X)V_f + XV_g \tag{3.19}$$

and then finding mean density as the reciprocal of the mixture specific volume. In this expression the specific volumes can be replaced by the reciprocal of the tabulated densities. The specific volume of water is often negligibly small compared to that of steam so the first term of Eq. (3.19) can sometimes be neglected, depending on the circumstances.

As regards the actual data, the 1967 Formulation for Industrial Use was replaced by a 1997 Formulation for Industrial Use (IAPWS-IF97), although the differences are negligible for geothermal use. The complete formulations divide the pressure–temperature space into regions, each with its own set of equations from which the properties can be calculated. The regions are shown in Fig. 3.6, reproduced from the publication by Wagner and Kretzschmar [2008].

For calculations where lower precision is acceptable in return for simpler numerical processing, IAPWS [1992] produced a set of equations describing the main property values along the saturation line, shown as region 4 in Fig. 3.6. These equations, which the IAPWS make available for unrestricted publication in all countries, are attached as Appendix A.

The compressibility of water is defined as

$$c = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{3.20}$$

and is needed for calculations of transient pressure changes in formations, Chap. 9. The compressibility of steam is less of a problem, as the properties of steam can be represented by $P/\rho = RT$ to acceptable accuracy, and the derivative substituted into Eq. (3.20). Values of water compressibility can be calculated from the expressions given for specific volume in IAPWS-IF97, region 1 in Fig. 3.6, but a simpler task for temperatures up to 100 °C and pressures to 1,000 bars abs would be to use the equations of Fine and Millero [1973] which are shown in Appendix B. Rogers and Mayhew [1967] also provide a data table showing the compressibility of water.

3.5 Hydrostatic Pressure and the Boiling Point for Depth Curve

It would not be wise to begin drilling a well in a known geothermal area without understanding the significance of hydrostatic pressure and what is known (in clumsy language) as "the boiling point for depth curve". The result would probably be an uncontrollable escape of any high-temperature water or steam that was intersected.

Hydrostatic pressure can be estimated roughly by assuming a density for water of 1,000 kg/m^3. (Although the word implies water, hydrostatic pressure is the name given to the pressure generated by a static column of any type of fluid.) The mass of a column of water 10 m tall and of cross-sectional area 1 m^2 would be 10^4 kg, and its weight would be g(10^4) or 9.81E4 kgm/s^2 (Newtons). The pressure exerted on the one square metre cross section would thus be 0.981 bars, a bar being 10^5 N/m^2, or approximately the equivalent of atmospheric pressure. In geothermal areas in particular, the temperature increases with depth, and since the density of water varies with temperature, it is more useful to describe the increase in pressure over an increment of depth *dz* as

$$dP = g.\rho(P,T).dz \tag{3.21}$$

from which the pressure at any depth can be calculated by integrating

$$P_z - P_0 = g\int_0^z \rho(P,T).dz \tag{3.22}$$

in which P_0 is the atmospheric pressure at the surface, where $z = 0$.

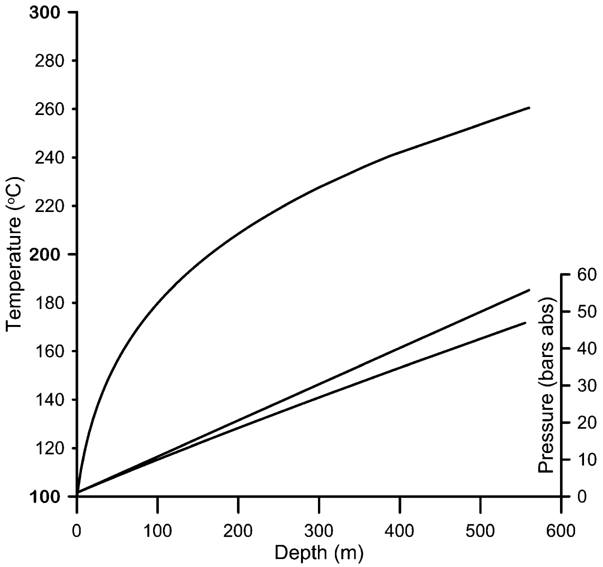


Fig. 3.7 Datum curves for hydrostatic pressure and the bpd curve

The variation of density with pressure and temperature is available as part of the IAPWS equations, so the variation of hydrostatic pressure with depth can be calculated for any given temperature distribution. The integration can be carried out using Simpson's rule or similar, for which the equation needs to be rearranged as

$$dz = f(P,T).dP = \frac{1}{g\rho(P,T)}.dP \tag{3.23}$$

A table of P_S as a function of z is given in Appendix C, calculated using the 1967 IFC Formulation for Industrial Use.

Two particular vertical pressure distributions are of interest, one with the well entirely cold, at surface temperature, and the other for the condition where the temperature variation with depth is such that the water is always just at its saturation pressure. These are shown in Fig. 3.7 as the two lower lines, using the right-hand axis. The upper of these two lines is straight, corresponding to the isothermal condition, which has a constant density for all depths; a temperature of 25 °C has been chosen, for which the density is 997 kg/m^3. The lower line is for the column being everywhere at saturation pressure, so the density decreases with depth because the temperature is increasing and the pressure falls progressively below the isothermal case with increasing depth. Provided the fluid is everywhere liquid, any measured vertical pressure distribution should fit between these limiting pressure cases if the water level is at the surface.

Having calculated the pressure distribution corresponding to saturation conditions at every depth, the matching temperature distribution can be found from a table (see Appendix C) or an equation giving P_s versus T_s, and the result is plotted in the figure, using the left-hand axis. This is the "boiling point for depth curve" (bpd curve). The curve is steep at first, and the gradient decreases with depth towards the critical point. When interpreting downhole temperature and pressure surveys, measurements are usually plotted on a graph like Fig. 3.7 which already has these distributions drawn in as datum curves.

What is at issue here is the form taken by a column of fluid in equilibrium. In the atmosphere, a compressible fluid, a stable distribution has specific entropy constant with height, but the physical reasoning for this involves air being able to mix freely to achieve this state. The air is at the same specific entropy at all levels in a stable atmosphere and changes pressure isentropically as it moves up or down. In an entirely cased well, orders of magnitude deeper than its diameter, fluid circulation is restricted—studies of the open thermosyphon clearly demonstrate this—see Sect. 6.1. Filled with isothermal cold water, the equilibrium pressure distribution is the linear distribution of Fig. 3.7. In the search for an equilibrium distribution, a well filled with water everywhere at its saturation conditions so that P and T are the saturation pair is tightly defined, but would it be in equilibrium? Under these conditions, Eq. (3.23) becomes

$$dz = f(P_s).dP = \frac{1}{g\rho(P_s)}.dP \tag{3.24}$$

The integration of this equation does not involve temperature, and the bpd temperature distribution is found separately. The well must be cased, as any exchange of fluid with the formations would have an influence. Despite the elegance of the idea, the bpd is not physically realistic as an equilibrium condition, as can be seen by examining thermal conduction. The temperature distribution gives rise to a conductive heat flux:

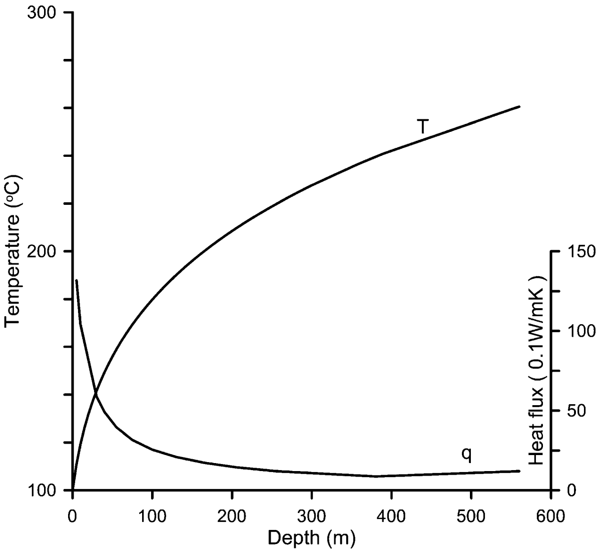
$$\dot{q}(z) = \lambda(P_s, T_s)\frac{dT}{dz} \tag{3.25}$$

The thermal conductivity, λ, at saturation conditions is a slowly varying function of temperature, and using the property data given by IAPWS [1998], the heat flux variation with z can be calculated. It is shown in Fig. 3.8 together with the bpd curve.

The heat flux increases towards the surface from about 400 m depth and below that increases for greater depths, more gradually. For the bpd distributions to represent an equilibrium state, the heat flux would have to be constant with z. This is in accordance with the general statement by Turner [1973] that Eq. (3.21) assumes no diffusion of heat or species in solution, the latter being the alternative to temperature as a means of producing density variations.

Despite these objections, some well measurements show temperature distributions which match the bpd curve, as will be demonstrated in Chap. 6. The reason is probably that the fluid in the well is two-phase but only just, with the dryness fraction almost zero. The steam would be present together with gas coming out of solution, as a few rising bubbles, sufficiently few that the liquid part of the column

Fig. 3.8 Boiling point for depth (bpd) curve and related heat flux distribution



remained continuous so that the hydrostatic pressure is the same as without any bubbles at all, the conditions of the bpd curve. For this to be the case, the bubbles would need to be small, so as to provide negligible drag on the water column—upward lift would reduce the hydrostatic pressure gradient. If the volume occupied by the bubbles increased, the liquid column would become narrower, sinuous, and eventually discontinuous, it would be subject to lift, and the hydrostatic pressure distribution would be different. There would be a whole spectrum of possibilities, of which a narrow range will match the bpd curve. Within this range, the heat flux in the column with a bpd temperature distribution would always be upwards and greater than the values shown in Fig. 3.8.

The bpd curve is nevertheless an important datum against which to compare steady-state well measurements.

References

Dugdale JS (1966) Entropy and low temperature physics. Hutchinson University Library, London

Fermi E (1956) Thermodynamics. Dover (copyright 1936)

Fine RA, Millero FJ (1973) Compressibility of water as a function of pressure and temperature. J Chem Phys 59:10

IAPWS (International Association for the properties of Water and Steam) (1998) Revised release on the IAPWS Formulation 1985 for the thermal conductivity of ordinary water substance. London, England

IAPWS (International Association for the Properties of Water and Steam) (1992) Revised supplementary release on saturation properties of ordinary water substance. St. Petersburg, Russia (http://www.iapws.org)

Perrot P (1998) A to Z of thermodynamics. Oxford University Press, Oxford

Pippard AB (1961) The elements of classical thermodynamics. Cambridge University Press, Cambridge

Rogers GFC, Mayhew YR (1967) Engineering thermodynamics, work and heat transfer. Longmann, London

Spielberg N, Anderson BD (1987) Seven ideas that shook the Universe. Wiley, New York

Turner JS (1973) Buoyancy effects in fluids. Cambridge University Press, Cambridge

Wagner W, Kretzschmar H-J (2008) International Steam Tables – properties of water and steam based on the industrial formulation IAPWS- IF97. Springer, Heidelberg