

The followings is part of Chap 1 taken from Kent W. Mayhew's 2018 book titled "New Thermodynamics: Say no to entropy"

System Parameters

If a volume of space contains matter and/or energy, the state of that space can be thermodynamically defined using the following five fundamental parameters, and their corresponding Systeme International d'Unites (S.I. units):

- 1) Entropy (S), S.I. units J/K
- 2) Absolute Temperature (T), S.I. units K
- 3) Pressure (P), S.I. units N/m^2
- 4) Volume (V), S.I. units m^3
- 5) Internal Energy (ε), S.I. units J

Entropy (S) and absolute temperature (T) are referred to as the thermal parameters, while pressure (P) and volume (V) are mechanical parameters. A system containing energy and/or matter can have a real or an imaginary boundary with the *surroundings* encompassing everything that envelops that boundary. Accordingly, a system can be arbitrarily or realistically drawn, such that it encloses all energy and matter of interest. Generally, a system should be drawn on a scale, such that all parameters of relevance can be construed as being homogeneous throughout the system.

How one defines a system depends upon the problem at hand. For example, an engineer may want to know the power requirements of a refrigerator with the refrigerator as a whole being considered as a single system, while the power being the rate at which energy is supplied. If the primary interest is the refrigerator's compressor, then the compressor can be considered as being a system and the remainder of the fridge becomes either a separate system or its surroundings.

Intensive parameters are independent of the system's size, while *extensive* parameters are proportional to the system's size. Generally, temperature and pressure are homogeneous throughout a system, i.e. intensive parameters. Conversely, volume, entropy and internal energy, all depend upon the system's size and hence are extensive parameters. Intensive versus extensive is not limited to the above five parameters, e.g. density and specific heat (per gram) are intensive parameters. Extensive parameters are additive, while intensive are not.

Intrinsic properties are parameters that define a system. Capital letters are used for intrinsic properties that represent the whole system. For intrinsic properties that are expressed on a per molecule basis, convention dictates that small letters are used. For example " V " represents the total volume of a system, while " v " represents the molecular volume within that system. Properties deemed *extrinsic* are only written in their capital letter form.

Defining a System

Any system in equilibrium has a pressure, volume and internal energy, which correlates to entropy multiplied by temperature via the following *parameter*

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relation^{7,8}:

$$TS = \varepsilon + PV \quad 1.1$$

The concept that temperature multiplied by entropy really has its basis with Clausius' mid-19th century assertion. Both TS , and PV , are defined in terms of units of energy, i.e. the joule:

- 1) Units for TS : $\text{K}(\text{J}/\text{K}) = \text{J} = \text{joule}$
- 2) Units for PV : $(\text{N}/\text{m}^2)(\text{m}^3) = \text{Nm} = \text{J} = \text{joule}$

Traditional: Eqn 1.1 defines the relationship among these parameters in terms of energy.

Internal Energy, Pressure & Volume

Volume is readily understood in terms of its three dimensional construct, as taught in grade school. Pressure in atmospheres is based upon the force that a 76 cm column of mercury exerts upon 1 square cm cross-section at 45 degrees latitude on the Earth's surface.

The internal energy (ε) is taken to be the energy associated with the microscopic random disordered motions of the atoms and/or molecules within a system. This traditional perspective is sometimes referred to as the "invisible microscopic energy".

Problematic concern A: *Seemingly eqn 1.1 implies that the energy of a system is defined in terms of the microscopic energy plus any macroscopic work as defined by PV change. Which sounds great until you ask the following: Should the macroscopic energy of a system not simply be a result of the summation of the system's microscopic energies?*

Temperature & Entropy: Traditional vs Our new Perspective

Everyone has felt hot and cold materials thus providing us with a qualitative understanding of temperature, which can be quantitatively measured by using a thermometer. When a thermometer reaches *thermal equilibrium* with the system, then it is the thermometer's *thermometric property* that has changed allowing the measurement of the system's temperature. Quantitative temperature will be revisited.

In the 19th century, Rudolf Clausius realized that something when multiplied by temperature represented energy. Since then, *entropy* has taken on an array of various meanings. To many its definition (wrongly?) revolves around the 20th century consideration that entropy signifies a system's disorder; essentially entropy represents the "randomness of matter in incessant motion"². An early 21st century but equally suspect definition is that entropy is "the dispersal of a system's molecular energy"³. A more recent yet still suspect definition belongs to Atkins⁴ "S is a measure of the quality of that energy; low entropy means high quality, high entropy means low quality".

Problematic concern B: *Entropy remains the poorest understood parameter,*

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specifically "no one knows what entropy really is"⁵, which is part of Von Neumann's statement to Shannon when Shannon was trying to figure out what to call a variable in his information theory.

Types of Systems

Three fundamental types of systems exist, each dependent upon the nature of our system's boundary and how energy and matter both flow across its boundaries:

- 1) An open system occupies a particular region of space from or into which both mass and/or energy may cross the system's boundaries;
- 2) An isolated system contains a fixed quantity of both energy and matter;
- 3) A closed system contains a fixed quantity of matter. Closed systems have two further breakdowns:
 - a) Adiabatic boundary whereupon there is no heat exchange.
 - b) Rigid boundary through which no mechanical work can be exchanged.

Thermodynamic Change

Thermodynamics concerns the correlation of the changes (Δ) to the five parameters that define a system's state, during some process. Therefore, a process can be defined in terms of some combination of: $\Delta S, \Delta T, \Delta P, \Delta V$, and $\Delta \epsilon$. We accept that momentarily transition states may exist, which may not be readily defined. Our concern becomes the transition between *equilibrium states* where eqn 1.1 is valid.

Changes to a system's state can be written as:

$$T_f S_f - T_i S_i = \epsilon_f - \epsilon_i + P_f V_f - P_i V_i \quad 1.2$$

where the subscripts "f" and "i" respectively represent the system's final and initial state.

Eqn 1.2 can be rewritten using the mathematical symbol delta (Δ), as follows:

$$(T_i + \Delta T)(S_i + \Delta S) - T_i S_i = \Delta \epsilon + (P_i + \Delta P)(V_i + \Delta V) - P_i V_i \quad 1.3$$

Multiplying through and collecting the terms, gives:

$$S_i \Delta T + T_i \Delta S + \Delta T \Delta S = \Delta \epsilon + V_i \Delta P + P_i \Delta V + \Delta P \Delta V \quad 1.4$$

Fig 1.1 graphically illustrates an increase to all the system's parameters. If all parameters are increasing then all deltas (Δ) in eqn 1.4 are positive.

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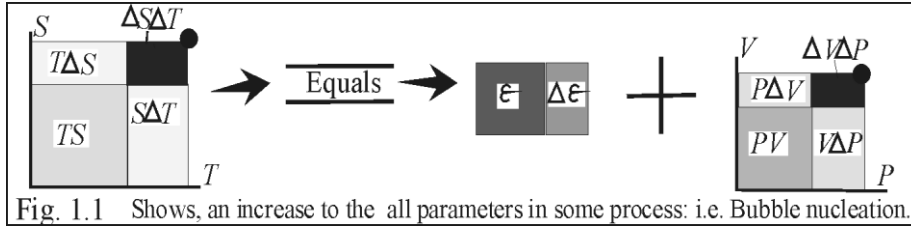


Fig. 1.1 Shows, an increase to the all parameters in some process: i.e. Bubble nucleation.

In the limit of thermodynamic change being infinitesimally small, then: $\Delta S \rightarrow 0$, $\Delta T \rightarrow 0$, $\Delta \varepsilon \rightarrow 0$, $\Delta P \rightarrow 0$ and $\Delta V \rightarrow 0$. Therefore, $\Delta S \Delta T \lll S \Delta T$, and/or $\Delta S \Delta T \lll T \Delta S$. Similarly, $\Delta V \Delta P \lll P \Delta V$, and/or $\Delta V \Delta P \lll V \Delta P$. Using these approximations, eqn 1.4 becomes:

$$S \Delta T + T \Delta S \approx \Delta \varepsilon + V \Delta P + P \Delta V \quad 1.5$$

Eqn 1.2 can also be written in differential form:

$$d(TS) = d\varepsilon + d(PV) \quad 1.6$$

For infinitesimally small change, eqn 1.6 can be approximated by:

$$T dS + S dT \approx d\varepsilon + P dV + V dP \quad 1.7$$

It is important to recognize that eqn 1.7, as the differential equation of eqn 1.2, remains valid if, and only if, the system's parameters changes are infinitesimally small, i.e.: $dS dT \lll S dT$, $dS dT \lll T dS$, $dV dP \lll V dP$ and/or $dV dP \lll P dV$. Situations exist where parameter changes are not infinitesimally small hence a more accurate result is obtained using eqn 1.2, rather than eqn 1.7. Consequentially, eqn 1.2 remains the general relation and the approximation is eqn 1.7!

Enthalpy

Enthalpy (H) is based upon PV space, and is defined as^{7,8}:

$$H = \varepsilon + PV \quad 1.8$$

Changes to enthalpy can be written:

$$\Delta H = \Delta \varepsilon + \Delta(PV) \quad 1.9$$

Rewriting eqn 1.9 in differential form:

$$dH = d\varepsilon + d(PV) \quad 1.10$$

For an *isenthalpic* system (constant enthalpy $\Delta H = 0$) eqn 1.9 becomes:

$$\Delta \varepsilon = -\Delta(PV) \quad 1.11$$

For isenthalpic systems any changes to internal energy ($\Delta \varepsilon$) is countered by changes to PV space ($\Delta(PV)$). The differential form of eqn 1.11 is:

$$d\varepsilon = -d(PV) \approx -(P dV + V dP) \quad 1.12$$

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Problematic concern C: *One cannot help feel that the real benefit of enthalpy is that it allows the science to bypass the poorly understood parameter known as entropy*

Simplified Systems

It is easiest to deal with *simplified systems* wherein certain parameters remain constant, while the others are system variables. Such systems are known as one of the following^{7,8}:

- 1) *Isobaric system:* A constant pressure system ($\Delta P = 0$).
- 2) *Isothermal system:* A constant temperature system ($\Delta T = 0$).
- 3) *Isometric (Isochoric) system:* A constant volume system ($\Delta V = 0$).
- 4) *Isentropic system:* A constant entropy system ($\Delta S = 0$).

For an isobaric process ($dP = 0$), eqn 1.7, becomes:

$$TdS + SdT = d\varepsilon + PdV \quad 1.13$$

If the process is also isothermal ($dT = 0$), eqn 1.13, becomes:

$$TdS = d\varepsilon + PdV \quad 1.14$$

Obviously, eqn 1.14 is a subset of the general relation, for isobaric and isothermal processes. Note: Traditionally, a convoluted approach is used by starting off with eqn 1.14 and then deriving all thermodynamic relations via various transformations (See Chapter 15).

To calculate isobaric & isothermal changes to internal energy ($d\varepsilon$) eqn 1.14 becomes^{7,8}:

$$d\varepsilon = TdS - PdV \quad 1.15$$

For the case of an isobaric & isothermal process wherein the system's internal energy remains constant ($d\varepsilon = 0$), eqn 1.14 simplifies to:

$$TdS = PdV \quad 1.16$$

For an isentropic process ($dS = 0$), eqn 1.7 becomes^{7,8}:

$$SdT \approx d\varepsilon + PdV + VdP \quad 1.17$$

If the above process was also isobaric then:

$$SdT \approx d\varepsilon + PdV \quad 1.18$$

Keeping certain parameters constant and others as variables can be continued resulting in an array of simplistic differential equations, as will be discussed in Chapter 16.

In this Book

It will be clearly shown that the work done (PdV) by the system is external to the system i.e. often the system's surroundings. Hence the change to internal energy is

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really the change to system's energy, while PdV actually describes work done to the surroundings through an expanding system's wall. This will alleviate many of the above described problematic concerns. Note: Many texts⁶ actually wrongly consider that work is done into a system's walls irrelevant of the walls being real or imaginary. Although this wrong consideration is a mathematically plausible the reality is that such math actually show that the work is through the walls^{8,9}.

Ideal Gas

An ideal gas is one wherein the gas molecules have no intermolecular bonding hence the bonding energy is zero: $U=0$. Note: Traditionally the bonding energy is taken to be part of the internal energy. Therefore, changes to an ideal gas's internal energy are also considered zero, i.e. $d\varepsilon= dU=0$. Real gases tend not to be ideal due to electromagnetic attraction, or repulsion between molecules in the gaseous state. Two examples being:

- 1) Polar gas molecules behave like magnets floating in space; hence they have an attraction to their neighbor's dipole moments, e.g. vaporous water molecules.
- 2) Similarly charged ionized gaseous molecules have an electromagnetic repulsion rather than attraction.

The mathematics of the energy associated with bonding of polar molecules is discussed in Appendix A.1 and are often dealt with using van der Waals' and/or Clausius' equation. The bonding potential (U) is attributed to the electromagnetic attraction between molecules, which decreases as the intermolecular distance increases. Sufficiently dilute gases at most temperature regimes sufficiently above their boiling points often can be approximated as ideal gases. Note: Hard to condense gases i.e. CO, H₂, N₂, O₂, tend to best approximate ideal gases¹.

If $dU \approx 0$, then simple compression or expansion of the gas by an external force does not alter the energy associated with that gas. Hence, for such an ideal gas under compression or expansion:

$$PV = \text{constant} \qquad 1.19$$

Robert Boyle (1627-1691) was the first to envision the fundamental principle that PV equates to a constant for an ideal gas being compressed or expanded by an external force; therefore, eqn 1.18 is known as *Boyle's law* (1660) and is sometimes also called *Boyle-Marriotte law*. Since PV remains constant during either compression or expansion, it follows that for infinitesimal change:

$$PdV = -VdP \qquad 1.20$$

The ideal gas law is commonly written in various forms, one being^{7,8}:

$$PV = nRT \qquad 1.21$$

where n is number of moles, and R is the ideal gas constant or $R = 8.31 \text{ J/mol}\cdot\text{K}$

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The *equation of state* for an ideal gas considers the microscopic energy of each molecule, and as such, is written^{7,8}:

$$PV = NkT \quad 1.22$$

where N is the number of gaseous molecules in the volume, (V) and k is Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J/K.

The impact of infinitesimal change to pressure and/or volume within a closed system containing an ideal gas can be calculated by differentiating eqn 1.22:

$$d(PV) \approx PdV + VdP \approx NkdT \quad 1.23$$

Both N and k are constants for an ideal gas system, therefore for isothermal expansion or compression: $dT = 0$ and $PdV = -VdP$, satisfying equations 1.19 through 1.22. Conversely, for non-isothermal processes then $dT \neq 0$ and $PdV \neq -VdP$. Accordingly, Boyle's law is actually limited to isothermal processes!

In this Book

It will be shown that the ideal gas law is a law with limitations that previously were misunderstood!

Quantitative Temperature

The quantitative nature of temperature is measured with a thermometer. Constant pressure and/or volume thermometers, both of which use a gas as the *thermometric medium*, are what all other thermometers are compared to. This includes modern electronic devices with digital readouts. Understandably temperature can be readily defined for temperatures ranges at which gases obey the ideal gas law. Specifically, for ideal gases their volume changes at a rate of 1/273 per degree Celsius temperature change.

Accordingly, the concept of temperature can be accurately measured at all temperatures except those approaching absolute zero. Absolute zero cannot be readily measured rather it is extrapolated to be negative 273 degrees Celsius. Hence absolute zero is somewhat arbitrary, and for many it is taken to be an entropy/second law based construct. Simply put absolute zero is the temperature at which an ideal gas of finite volume has no pressure, or if you prefer the temperature at which vibrational energies within condensed matter ceases to exist..

The measurement of temperature requires a scale so that comparisons can be made. In 1745, Carolus Linnaeus decided that 0°C, and 100°C would respectively represent the freezing, and boiling points of water, thus creating the Centigrade scale. In 1948, the Centigrade scale was dropped in favor of using degrees Celsius.

In 1887, P. Chappuis studied constant volume

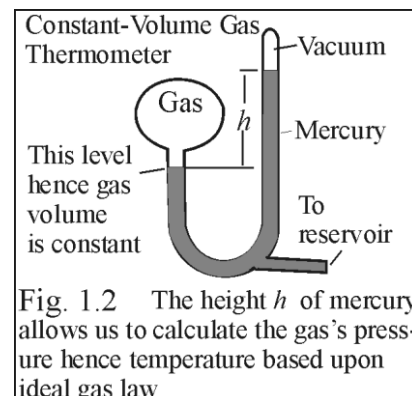


Fig. 1.2 The height h of mercury allows us to calculate the gas's pressure hence temperature based upon ideal gas law

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thermometers, where a gas residing in a glass bulb, acts as the thermometric medium, meaning it is placed in thermal contact with the system whose temperature is being measured. As shown in Fig. 1.2, the gas's volume is held constant by either adding, or subtracting, mercury through the tube labeled "to reservoir".

By knowing the density of the mercury in the tube, the gas's pressure is readily calculated by measuring the height (h) of mercury inside of the tube. Knowing the gas's pressure and constant volume, the temperature is then calculated using the ideal gas law, i.e.:

$$T = PV / Nk \qquad 1.24$$

One does not necessarily need to know the number of molecules (N) in order to utilize a constant volume thermometer. You could compare the ratio of temperatures for two systems in terms of their pressure ratio, i.e. $T_1/T_2=P_1/P_2$, and knowing one of the system's temperatures then enables one to measure the other system's temperatures.

Quantitative Temperature is really a comparative

When measuring the temperature of a system, the thermometer is placed in thermal contact with it. Thermal equilibrium is obtained when the influx equals the efflux of thermal energy between the thermometer and the system whose temperature is being measured.

If two systems in thermal contact are at the same temperature then the net exchange of thermal energy between them would be zero. This is the basis of what is known as the *zeroth law* of thermodynamics, which treats *thermal equilibrium* as a transitive property. Two systems are considered to be in thermal equilibrium with each other, if the following two conditions, hold true^{7,8}:

- a) both systems are in an equilibrium state; and
- b) both systems remain in equilibrium when they are brought into thermal contact.

As a transitive property the zeroth law states that *thermal equilibrium exists*^{7,8}: "*If two systems/bodies are in thermal equilibrium with a third, then they must be in equilibrium with each other.*" Intuitively, the third system may be considered as being a thermometer.

The zeroth law of thermodynamics can be considered as similar to, but slightly different than the first law of thermodynamics that being the fundamental principle that energy is conserved, i.e. energy can be converted from one form to another, but it cannot be created nor destroyed. Accordingly, the total influx of energy into a system must equal the energy change within that system minus the magnitude of the efflux of energy out of that system.

For a given substance or system, its thermal energy density is directly proportional to its temperature for most temperature regimes experienced here on Earth. This does not mean that a thermometer compares the thermal energy densities

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because different substances in different states all have different thermal energy densities. Although differing systems have differing thermal energy densities at a given temperature, their temperature always defines the net direction of flow of heat that being from hot to cold.

Temperature can also be taken as a comparative between systems and/or as to what is felt when standing outside on Earth, where the thermal energy density is primarily derived from our Sun. Interestingly, when a system is in thermal contact with our atmosphere, then that system generally exchanges thermal energy with our atmosphere whose thermal energy density was primarily attained from the sun. This is fundamental to so many phenomena in part because our atmosphere often acts as the mother of all heat baths/sink/reservoir. Remember, thermal equilibrium means that the systems are at the same temperature in which case the systems are exchanging equal amounts of thermal energy.

Thermal Energy

In condensed matter, the molecules are so close that electromagnetic (EM) intermolecular bonds exist between all the molecules. When considering systems of condensed matter, the *thermal energy* is contained within the vibrations associated with both the intermolecular and intramolecular bonds. Specifically, *intermolecular vibrations* are between molecules, while *intramolecular vibrations* are between the various atoms that constitute the molecules.

Phonons are packets of energy related to the random lattice vibrations in solids, which are a function of the crystalline substance's temperature. Phonons are theoretical equivalent to photons. Specifically, a phonon is an electromagnetic (EM) particle within a crystalline substance, while a *photon* is an EM particle in *freespace* that being a volume without matter. Since crystalline substances have a lattice structure that prefers specific phonons, our expectation is that crystalline substances preferentially interact with specific frequencies of photons.

Liquids and amorphous solids lack the crystalline structure to which phonons are mathematically related. Even so, it is accepted that the thermal energy contained within such substances can be considered as phonons (packets of energy) that are treated in the same manner. Liquid molecules also have freedom of movement (e.g. convection), and accordingly they can possess both translational and rotational energies. However, both of these energies are generally considered to be minor in comparison to vibrational energy. Therefore, most of the thermal energy within all condensed matter can be attributed to vibrational energy.

A more exacting deliberation would include the fact that changes to a system's energy results in changes to the vibrational energy, which in its simplest terms can be thought of as the motions of intermolecular and intramolecular EM bonds. Such motions transform vibrational energy into photons. Equally, photons that interact with matter as thermal energy can be transformed into the movement of molecular EM bonds.

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Any analysis should consider that most condensed matter absorbs and emits thermal energy, which for the most part consists of photons whose frequencies are less than that of light. Moreover, the hotter the matter is the more thermal radiation it emits, which is the basis of thermal imagery devices such as infrared military night goggles.

Visible light

Visible light is EM radiation generally at slightly higher frequencies than thermal energy. Certainly color in matter implies the absorption of certain frequencies and the reflection of others. Note: Many adsorbed frequencies may contribute as heat. An interesting consideration; can light actually be seen with our eyes? Light in space remains invisible to our eyes, it is only when it interacts with matter that we actually see it! For example a light ray through dust/smoke is visible but that same ray through a vacuum is not so discernable. Similarly, it is only when light reflects off of, or refracts through matter that its presence is actually revealed by our eyes. For an interesting and controversial take see/google Goethe's theory. This does not necessarily mean that darkness is anything but the absence of the light, as Goethe's would believe. Rather I believe that this has more to do with how our eyes evolved. Imagine that all rays of light were seen then we would be blinded by those rays. Thermal (infra-red) imagining is really a just a wavelength shift by a device, enabling our eyes to see the energy that has interacted with, and is now being emitted by warm/hot bodies of matter. Food for thought.

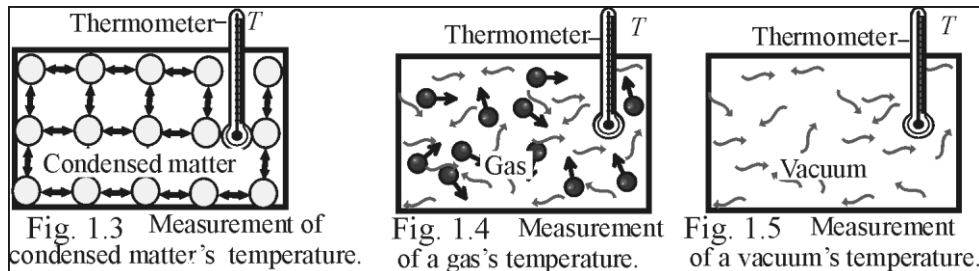
Measurement of Temperature

For condensed matter, temperature is considered as being a measurement of the vibrational energy associated with the kinetic motions of the system's molecules, i.e. the system's kinematics. Such an interpretation becomes problematic when considering gases.

Consider the measurement of the temperature of a gas, as is illustrated in Fig. 1.4. Obviously, thermal energy is transferred between the thermometer and the volume of gas, via a combination of:

- 1) The gas molecules physically exchanging their kinetic energy with the molecules within the thermometer through collisions with the thermometer; and
- 2) Thermal energy being absorbed from, and emitted into the surrounding freespace results in the exchange of thermal energy between the system and thermometer.

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The net result is that the molecules within the thermometer attain thermal equilibrium with the system. Again, thermal equilibrium occurs when both the thermometer and gaseous system have an equal influx vs efflux of thermal energy.

Temperature Consideration

Problematic concern D: *Strangely, traditional thermodynamics only considers temperature in terms of a system's kinematic, which is fine for condensed matter Fig 1.3. Can the above described thermal radiation [2]) simply be ignored when contemplating temperature? Certainly the total energy associated with thermal radiation often is minute when compared to other thermal energies within a given system.*

The problem becomes most obvious when one considers a vacuum, as is illustrated in Fig. 1.5. The traditional interpretation is that a matter-less vacuum possesses no molecular motion, and hence has no temperature i.e. zero kinematics of matter thus has no temperature. Strangely however, if a thermometer is placed into such a vacuum containing thermal radiation, then the thermometer obtains a temperature reading, solely due to the exchange of thermal radiation. Specifically, the molecules within the thermometer eventually attain thermal equilibrium with the surrounding thermal radiation, although no kinetic energy actually existed within the vacuum until the thermometer was placed inside.

A metaphysical argument arises. Traditionalists argue that by putting a thermometer into the vacuum, there is now a temperature associated with the thermometer but not with the surrounding vacuu but is the thermometer not actually measuring the vacuum's temperature? E.g. consider that a thermometer is put into an immense vacuum that is full of thermal radiation. Although the energy associated with thermal radiation is often minute when compared to the energy of molecular kinematics, the fact that the vacuum's volume is immense means the eventual thermometer's temperature reading will be that a of the vacuum. Furthermore, because the speed of light is vast, a significant quantity of heat can be exchanged within a vacuum even when the thermal radiation density in that vacuum remains diminutive in comparison to thermal energy contained within most condensed matter.

Consider the dark side of the moon being much colder than the bright side! It

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seems farcical that the word "cold" is used if it no longer applies to relative temperatures. Certainly, the moon's condensed matter involves kinematics. What about a few millimeters above the moon's surface? Does the term temperature no longer apply? Are we to believe that there is no thermal equilibrium between the matter on the moon and the space that surrounds it?

Arguably clarity could be obtained by saying: If a thermometer makes a measurement in a system, then that system has a temperature! However this too may be problematic because a better understanding of thermal radiation is needed. This should make more sense after reading the ensuing chapters.

Certainly at a given temperature, systems containing matter:

- 1) Will tend to exchange thermal energy faster than vacuums; and
- 2) Will have a higher thermal energy density than freespace i.e. matter tends to concentrate thermal energy and hence increase the thermal energy density within a given volume.

The general exception occurs when we are dealing with thermal radiation at high temperatures, i.e. "radiation heat transfer", for which significant heat exchange can occur even through a vacuum, e.g. systems at blast furnace type temperatures.¹¹

Conclusion at this point traditional thermodynamics should reconsider its stance concerning temperature. Of course their argument goes beyond the energy associated with kinematics often being significantly greater than that associated with radiation. Specifically, it is based upon the traditional insistence that probability/mathematical based statistical thermodynamics is more relevance than common sense, e.g. another case of maintaining the second law as some supreme postulate.

In this Book

It will be demonstrated that the accepted limiting temperature to the kinematics of matters is wrong!

Joule's Gas Expansion Experiment

The experiment illustrated in Fig 1.6 and 1.7 is known as Joule's experiment for gases. James Prescott Joule concluded that since no temperature change was found in the heat bath that his experiment shows that the gas's internal energy is a function of temperature but not volume. Joule's experiment is far from perfect, e.g. if energy were extracted from the surrounding heat bath then would it be measurable? Even so, it has been verified by others performing more exacting experiments e.g. Lord Kelvin's version of Joules' experiment. Obviously the isothermal expansion of an ideal gas implies that $d\varepsilon = 0$.

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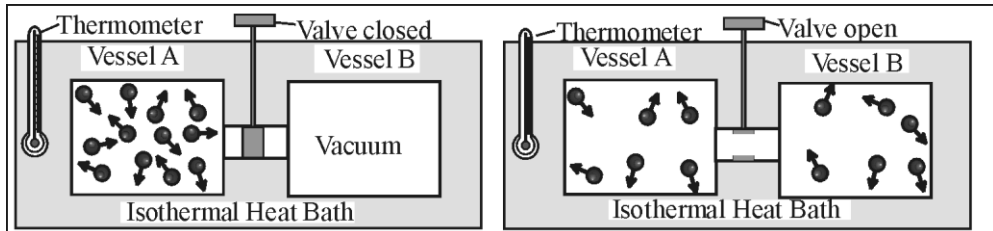


Fig 1.6 Shows a dozen moving molecules in an isothermal system separated from an equal volume isothermal vacuum, by a closed valve. A.K.A.: Joules experiment.

Fig 1.7 Shows the same dozen molecules of Fig 1.6, with the valve opened allowing for the molecules to disperse evenly between both Vessel A and Vessel B.

Ideal gas Paradox

Problematic concern E: Bearing in mind the previously stated definitions of entropy, consider the ideal gas in Vessel A, as shown in Fig 1.6. A valve is opened and the gas is allowed to isothermally disperse into Vessel B, as is illustrated in Fig 1.7. We expect that $PdV = -VdP$. In other words, as the gas's volume doubles its pressure decreases by half.

As this ideal gas's volume increases, the molecules' randomness, and/or the dispersal of energy, must increase. Therefore by certain definitions, its entropy should increase ($S \uparrow$). If a system's entropy is increasing, and there is no total energy change within the system, then shouldn't we expect that the ideal gas's temperature will decrease ($T \downarrow$), such that: $TdS = -SdT$? But that makes no sense because the process is isothermal ($dT = 0$), allowing Boyle's law (Boyle-Mariotte law) to remain valid, i.e.: $PdV = -VdP$. Certainly, if the internal energy is related to the potential associated with intermolecular bonding, then the ideal gas's internal energy does not change.

Seemingly, there is something wrong with Joules' understanding. What could it be? Perhaps the ideal gas law is only an approximation! One could rightfully argue that the heat bath kept everything isothermal, but the above experiment should remain isothermal without the heat bath. Other possibilities:

1) Perhaps, we must reconsider eqn 1.7: $TdS + SdT = d\epsilon + PdV + VdP$

If $PdV = -VdP$ and $dT = 0$, then 1.7 implies:

$$TdS = d\epsilon \quad 1.25$$

If eqn 1.25 defines changes to our isothermally expanding ideal gas, then one cannot isothermally expand a gas and maintain constant internal energy within that system of gas. In which case the internal energy of our isothermally expanding ideal gas has seemingly increased: ($d\epsilon \uparrow$). Does this mean that the internal energy changes, while the intermolecular bonding energy remains constant, as expected for an ideal gas? It all seems convoluted.

2) Perhaps we must reconsider what entropy is!

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Since: $PdV = -VdP$ and $dT = 0$, and if $d\varepsilon = 0$, then $dS = 0$. Consider our previously given two definitions of entropy. During the isothermal expansion of the ideal gas, both the randomness of molecules in incessant motion and/or the dispersal of the gas molecules energy have increased, yet there is no predicted entropy change? Seemingly, the virtues of entropy should be queried! Has Atkin's consideration of the quality of the energy changed? Perhaps but even that remains weak!

Ultimately the ideal gas law has suffered a paradox. One might argue that our analysis is overly- simplistic. But to do so implies that the ideal gas is complex, which it is not. Or that eqn 1.1 cannot be obtained by the integration of eqn 1.14. And herein resides the issue.

In order to circumnavigate the above logic, thermodynamics may have unwittingly complicated the simple, in part by shuffling the differential equations around, all in order to protect the false postulate.

In this Book

It will be discussed that Joule's experiment really only demonstrates that no work can be done onto a vacuum! I.e. it shows that the expansion into a vacuum does not change the energy of gas. In context of entropy; if this had anything to do with randomness of molecules, then randomness has nothing to do with energy of gas. It will be shown that much of our 20th century teachings has been fool's gold all because the science remained postulate blind

Heat Transfer

Thermodynamics concerns the transfer of thermal energy (heat) both into, and out of, a system. Such heat transfer is could be dealt with in terms of TS space, where entropy (S) is considered in its simplest guise: Entropy is something that when multiplied by temperature defines thermal energy, hence isothermal entropy change is often traditionally defined the Clausius equation, which is commonly written in the following form^{6,7}:

$$\Delta S = \Delta Q / T \quad 1.26$$

Where ΔQ is the thermal energy (heat) change. Eqn 1.26 can be rewritten:

$$\Delta Q = T\Delta S \quad 1.27$$

From a purely mathematical perspective, eqn 1.27 implies that the thermal energy change (ΔQ) is directly proportional to the entropy change (ΔS), and that the proportionality constant is temperature (T).

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Problematic concern F: *There is a profound drawback to the Clausius equation; it does not consider the thermal energy change (ΔQ) in terms of temperature change (ΔT), but only entropy change (ΔS) i.e. it is an isothermal relationship. This bodes the question; what exactly is entropy? Answer remains the same no one really knows. Great!*

Moreover at first glance, it befuddles the mind concerning how does one have a thermal energy change within a system and no temperature change. To some the answer is; this applies to systems where influx (energy entering) equals the efflux (extracted energy). Certainly this limits the applicability of eqn 1.27.

To others the answer is somewhat more complex, in that infinitesimal changes are contemplated, i.e. energy exchanges that are too small to be measured by a thermometer as a temperature change (ΔT). The reality remains that ΔT is only not noticed because the thermometer is not accurate enough to read such a minuscule ΔT . This is NOT exactly the same as $\Delta T = 0$.

The above absurdity is further hidden by traditional claim that these concepts are developed based upon heat reservoirs i.e. the definition of a heat reservoir/bath/sink being a system wherein exchanges of thermal energy do not alter its temperature! Again just because temperature change was infinitesimal, does not mean it did not occur!

Think back to previously discussed Joule's experiment. Joule rendered his conclusion based upon the fact that in his experiment the heat bath's temperature did not change. Certainly any energy associated with the expanding gas should be infinitesimally small compared to the heat bath's thermal energy. It is hard to fathom why, after Joule's experiment that none jumped all over the dangers of developing a science based upon such consideration of infinitesimals.

Ultimately, eqns 1.26 and 1.27 are based upon the rather poor conceptualization of an isothermal system's thermal energy change. Or, does the exchange between heat reservoirs simply mean that the equations do not apply to real systems, where thermal energy changes are noticeable? Any way you look at it, this is another consequence of formulating a science around the second law as a postulate.

Ideal Gas Constant and Specific Heat/ Heat Capacity

Problems associated with Clausius equation can be avoided by thinking in terms of specific heats and/or heat capacities, which allows us to consider a system's thermal energy change in terms of temperature change. Why would anyone prefer Clausius's consideration over specific heat/heat capacity?

A problem with heat capacity being that it does not remain constant through all temperature regimes. Planck¹ discussed that a zero calorie was taken as the energy required to raise a gram of water from 0 to 1° C. And that

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this differs from what is taken to be an actual/mean calorie that being the energy required to increase one gram of water's temperature from 14.5 to 15.5° C, which equals 1/1.008 of a zero calorie. Seemingly this is a small difference, but it is also over a relatively narrow temperature range. Even so, considering heat capacity as a constant over most (not all) temperature regimes generally provides us with a useable approximation.

Overlooking the above problem, the preference lay in the fact that as traditionally written, isothermal entropy change fits well with statistical probability based conscripts which are used to defend the second law as a postulate. And are to this author are part of the traditional self-serving over complication of the science that is really embedded with circular logic.

Consider the specific heat per unit mass, where the subscript "y" describes the variable that is considered constant. The isobaric specific heat per gram (or per kilogram) (unit mass in SI system) for a given substance is⁷:

$$c_p' = (1/m)(dQ/dT)_p \quad 1.28$$

Similarly, the isometric specific heat per gram for a given substance, becomes⁷:

$$c_v' = (1/m)(dQ/dT)_v \quad 1.29$$

Similarly, the isobaric molar capacity for a given substance is⁷:

$$C_p = (1/n)(dQ/dT)_p \quad 1.30$$

Similarly, the isometric molar heat capacity for a given substance is⁷:

$$C_v = (1/n)(dQ/dT)_v \quad 1.31$$

The isobaric heat capacity is greater than the isometric heat capacity for a gas ($C_p > C_v$ or $c_p' > c_v'$). Specifically, the correlation between the molar isobaric heat capacity (C_p), and the molar isometric heat capacity (C_v), for an ideal gas is given by Mayer's relation⁷:

$$R = C_p - C_v \quad 1.32$$

For a monatomic ideal gas, the result of eqn 1.32 fits our empirical findings. Specifically, for such a gas $c_v \approx 3R/2$, and $c_p \approx 5R/2$. Eqn 1.32 is often rewritten in different formats, e.g.⁷:

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$$R = C_v(C_p / C_v - 1) \quad 1.33$$

which leads to⁷:

$$C_v = R / (C_p / C_v - 1) \quad 1.34$$

which can be rewritten as⁷:

$$C_v = R / (\gamma - 1) \quad 1.35$$

where γ is the *adiabatic index*⁷: $\gamma = C_p / C_v$, that being the ratio of heat capacities

In this Book

The explanation for the difference between the two heat capacities will become apparent in the ensuing chapters, namely Chapter 5, where it is association with work is discussed. Specifically, this difference is due to work done onto the surrounding atmosphere.

Thermal Conductivity

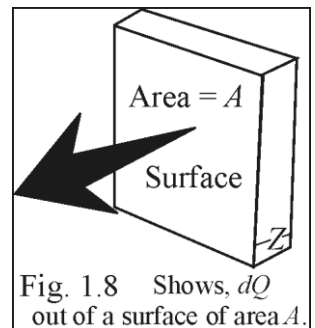
Thermal conductivity represents the ability of a system to transfer thermal energy. In order to better understand thermal conductivity, consider a surface with area A , as is shown in Fig. 1.8. Assuming it is not in temperature equilibrium therefore, heat is transferred through the surface at the rate given by⁷:

$$dQ / dt = -\kappa dT / dZ \quad 1.36$$

where T = temperature, t = time, κ = coefficient of thermal conductivity and dZ = thickness

Reversibility

Reversibility is an idealistic concept concerning a system's state, wherein a system in some process can readily return to its initial state. Processes are generally irreversible i.e. cannot return to their original energy state without an input of external resources, e.g. an input of energy. The fact that most processes are irreversible has consequences such as prevention of perpetual motion, which is traditionally wrongly explained in terms of entropy and its accompanying postulate, that being the second law. Furthermore, reversibility requires that all thermodynamic change be infinitesimal² that forms a basis of what is current dogma, which often removes the science from reality.



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In the ensuing chapters it will be shown that irreversibility of all processes can be explained without the requirement of the second law. Moreover this demonstrates that the second law is a false postulate.

First Law of Thermodynamic:

In terms of infinitesimals the first law can be written in terms of a system's internal energy change (du), the energy input (dq_{in}), and work done (dw) by the system, that being the combined law:

$$du = dq_{in} - dw = dq_{in} - Pdv \quad 1.37$$

du is positive when $dq_{in} > Pdv$. Conversely du is negative when $dq_{in} < Pdv$. Note: Writing $dw = Pdv$, means eqn 1.37 is limited to reversible work. Similarly, reversible heat is accepted as $dq_{in} = Tds$. For some reversible thermal energy input:

$$du = dq_{in} - dw = Tds - dw \quad 1.38$$

For isobaric processes the first law is traditionally accepted as:

$$du = dq_{in} - dw = Tds - Pdv \quad 1.39$$

Problematic concern G: *The inherent problem remains that neither eqn 1.37 nor 1.38 were for any real process because reversibility (mechanical or thermal) remains an idealistic rather than a realistic concept. Seemingly tradition asks us to accept that two wrongs make a right. Perhaps!*

Certainly one could argue that these are minor wrongs; however a wrong is never absolutely right! Moreover, the term law requires absolute! Another way of viewing this is reversibility is limited to quasi-static processes, which are not necessarily realistic processes.

In this book

It will be shown that irreversibility of all processes can be explained in simple terms with no reliance upon either entropy or the second law. Remember a basis of traditional thermodynamics is the use of second law to explain irreversibility, which will be shown to be a complication of reality all based upon a misunderstanding of lost work.

Problematic concern H: *Equating $dq_{in} = Tds$ is not exactly based upon any constructive logic rather it was defined that way by our 19th century greats. And through the 20th century we were told to embrace it. Yet any notion that this proves anything is nothing short of circular logic because it was defined as equality, rather than formulated upon constructive logic.*

Continuing eqn 1.39 gives:

$$Tds = du + Pdv \quad 1.40$$

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Substituting in for isometric specific heat (c_v), $du = c_v dT$ one obtains:

$$Tds = c_v dT + Pdv \quad 1.41$$

Problematic concern I: *Consider a process in which no work is done ($dw = 0$). This leads to the following trivial result: $dq_{in} = du$. This implies that when no work is done, then: $Tds = du = C_v dT$ which is not particularly comforting because isothermal entropy change is equated to isometric heat capacity (C_v) times temperature change. It is doable because nobody knows what entropy is therefore entropy change can be anything or perhaps even strange remain something for everything!*

Integrating when $dw = Pdv = 0$ gives: $dS = c_v dT / T$ which leads to natural logarithmic functionality.

Problematic concern J: *The inherent logic remains illusionary because, a constant temperature system is on one side of the equality, while a temperature change exists on the other side of the same equality. Similarly, constant volume on one side of the equality and entropy change on the other.*

Okay, logic be damned! Continuing, divide eqn 1.41 by T gives:

$$ds = c_v dT / T + Pdv / T \quad 1.42$$

For a mole of ideal gas molecules the ideal gas law leads to $P/T = R/V$. Hence:

$$ds = c_v dT / T + Rdv / v \quad 1.43$$

Integrating results in:

$$\Delta S = C_v \ln(T_2 / T_1) + R \ln(V_2 / V_1) \quad 1.44$$

One can see why mathematical entropy has been embraced. Overlooking the previously discussed fundamental problems, you may become beholden to this world of natural logarithmic functions, which fits so well with probability based statistical thermodynamics. As to what is entropy's true guise? Based upon eqn 1.44 no one really knows!

Problematic concern K: *Consider a process where work is done while the energy input is zero i.e. $Q_{in} = 0$. Since $dq_{in} = TdS$ therefore there is no entropy change, but how can that be? Is not entropy related to work by eqn 1.40? Are we to believe that this correlation only exists when the system's internal energy is constant? Talk about weak constructive logic!*

Problematic concern L: *Eqn 1.44 concerns entropy change and entropy is traditionally accepted as being valid over all temperature regimes. To many this has specific special meaning especially for temperatures approaching absolute zero where as previously stated our understanding of temperature becomes arbitrary. If temperature is arbitrary then based upon 1.44 so too is entropy. Moreover heat capacity, which is not constant over all temperature regimes, in all likelihood loses all meaning near 0 K.*

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Reconsider the enthalpy relation ($H = U + PV$). The combined first and second law are sometimes traditionally rewritten like the enthalpy relation as:

$$dh = du + d(PV) \approx du + Pdv + vdP \quad 1.45$$

Solving for du in eqn 1.40 and substituting into eqn 1.45 gives:

$$dh \approx Tds - Pdv + Pdv + vdP = Tds + vdP \quad 1.46$$

Eqn 1.46 is often referred to as the enthalpy relation or combined first & second law (b), or even Gibbs equation (b). It all looks grand except at certain levels what was conceived simply ignores fundamental issues, preventing the science from adhering to constructive logic.

In this Book

The above series of problematic concerns will be addressed. Furthermore the differences between a system's energy and its ability to do work will be addressed. I.e. putting energy and work in the same equation and then to claim that they have the same functionality to temperature may be irrational. It is like adding apples and oranges and not realizing that the answer is now in fruit. To the indoctrinated this may seem absurd but in the ensuing chapters the differences between a system's ability doing work, and its thermal energy, will be investigated.

Joules Weight Experiment

Another of Joules experiments involves weights on a rope that drive a series of paddles rotating on shaft in a liquid. Herein it was determined that work and energy are one and the same based upon the liquid's temperature increase as the weights dropped thus rotating the paddles in the liquid. This equality of work and energy is further backed by various mathematical analyses in most textbooks. And it is true that work and energy are often one and the same, but this is not always the case, as previously stated!

In this book

Joules claims that his experiment shows that all the work that is put into the system in his experiment was readily turned into thermal energy. Interestingly it will be determined that the converse is not necessarily true. Specifically all the energy of a system cannot be extracted as work. Furthermore, Joules experiment also shows is that increased motions in a liquid leads to heating of that liquid, which implies that intermolecular collisions are not elastic, as is traditionally taught. This too will be dealt with herein.

Joules Gas Expansion Experiment: Revisited

Reconsider Joules expanding gas into a vacuum experiment. Planck^{1pg51} discusses Lord Kelvin's version of this experiment, which is really a version of what is known today as a throttling process, where what he calls the external work done is defined

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by:

$$W = P_1V_1 - P_2V_2 \quad 1.47$$

Problematic concern M: Planck was willing to consider external work in terms of: $W = -d(PV)$.

In this book

The implication must be that work done can be defined in terms of PdV will be examined e.g. the ideal gas law relates to work. Again this simple relation is traditionally avoided to protect the postulate (second law), and this too will be discussed throughout this book as simpler understandings are presented!

Entropy Change in Heat Transfer

For reversible isothermal heat transfer, the following is traditionally used:

$$ds = dq_{rev}/T \quad 1.48$$

For path independent processes eqn 1.48 can be rewritten as:

$$\Delta S = Q_{rev}/T \quad 1.49$$

Problematic concern N: *The fact is that heat transfer is always from high to low temperature, and that this is fundamentally not reversible, unless the temperature difference is so infinitesimally small that it approximates zero. This seemingly separates such analysis from reality.* Continuing with traditional analysis; for two heat reservoirs in thermal contact hence exchanging thermal energy:

$$\Delta S = Q_{rev}/T_c - Q_{rev}/T_h = Q_{rev}(T_h - T_c)/T_hT_c \quad 1.50$$

Based upon eqn 1.50, the traditional claims are that heat must flow from hot to cold and that the net entropy change is always greater than zero. How constructive was the logic in getting to this point? There is no disagreement that the net flow of heat is always from hotter to colder but the traditional reasoning is disagreeable at so many levels.

Problematic concern O: *Eqn 1.50 requires reversibility between heat reservoirs, which limits its usefulness to systems whose temperature does not change during the given process. To further exasperate the situation the temperature difference must be real yet approximate zero! As a realistic applicable equation, eqn 1.50 remains suspicious at best*

In this Book

The reason two heat reservoirs were traditionally considered is simply because heat reservoirs contain so much heat that the extraction of some thermal energy can go unnoticed i.e. no measurable temperature change. The real reason that it is unnoticed is that thermometers tend not to be accurate enough to read minuscule temperatures changes associated with such thermal energy changes to heat reservoir,

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which is fundamental for a system to be considered a heat reservoir/bath. Just because temperature change is infinitesimally small, does not mean it did not occur! This book does not white-wash reality.

Traditional Free Expansion

Consider an expanding system or specifically the traditional writing for entropy change in the free expansion of a system (ΔS_{sys}) from state 1 to state 2:

$$\Delta S_{\text{sys}} = \int_1^2 ds = \int_1^2 dU/T + \int_1^2 PdV/T \quad 1.51$$

Since the process is unrealistically deemed isothermal, therefore: $dU=0$ and eqn 1.51 for a freely expanding system containing a mole of molecules becomes:

$$\Delta S_{\text{sys}} = \int_1^2 PdV/T = R \ln(V_2/V_1) \quad 1.52$$

The entropy increase as described by eqn 152 is to the expanding system itself. Sounds great, in part because it fits with the 20th century assertion that increases in randomness is associated with energy change.

Problematic concern P: *If the expanding gas is ideal and isothermal then based upon Boyle's law there is no change to the gas's energy. Therefore just because a gas has expanded does not mean that its energy has changed although one might argue that the gas's randomness has changed.*

It remains interesting that Ben-Naim⁵ rightfully points out that randomness is not a particularly scientific term because when describing randomness of various systems, the answer remains in the eyes of the beholder. Furthermore Planck¹ realized that work is often done onto the surrounding atmosphere. It just seems strange that Planck did not make/state the following connection.

Problematic concern Q: *Concerning eqn 1.52 traditionalists failed to recognize that in free expansion that there is an exchange of energy between the expanding system and its surroundings.*

In this Book

It will be discussed that expanding systems tend to do work onto their surrounding atmosphere and that this is generally lost work^{8,9}. In order to understand how free expansion has fooled thousands, all you need to realize is that it was conceived for quasi-static expansion. Thus for a system that does work, instead of cooling the expanding system's temperature, the expanding system remained isothermal because thermal energy is allowed to pass from the isothermal surroundings through the walls and into the expanding system. Moreover when discussing free expansion the expanding force is not always clearly defined, which

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has ramifications, as will be discussed throughout this book. This enables us to now understand the essence of this accepted gross misunderstanding!

Entropy and the Second Law

Herein, the conceptualization of entropy has already been challenged. What about the second law? The second law states that for any process, the isothermal entropy change of any isolated system is always equal to or greater than zero. And as previously stated this is traditionally used to explain why real life processes tend to be irreversibility!

Problematic concern R: *The second law loses its universal appeal because it is limited to ISOLATED systems. Few systems here on Earth are truly isolated. Specifically, any system that experiences a volume increase must displace its surroundings atmosphere, in which case it is NOT an isolated system. This clearly dethrones the second law as some universal supreme law i.e. **Second law** is a false postulate!*

Our reality; whether we are considering an expanding system powering a device, or a chemical reaction where the volume of the products surpasses the volume of the reactants, then we are considering systems that must displace our atmosphere's mass. To think of any other outcome is to claim that our atmosphere has no mass, or that its mass is not contained within Earth's gravitational field^{8,9}.

Accepting the equation written on Boltzmann's tombstone, then entropy can be defined by:

$$S = k \ln \Omega \quad 1.53$$

where Ω is number of microstates, k is Boltzmann's constant

In this Book

As previously stated the second law's absolute validity will be dethroned mainly by showing that simpler explanations exist for all that it is wrongly claimed to explain.

Is this not simply logical, that molecules experiencing continuous intermolecular collisions with tend to disperse? Of course constraints generally prevent complete dispersal. Furthermore, thermal energy (heat) also tends to disperse often resulting in the heating of cooler systems at the expense of the hotter systems. This is irrelevant of whether it is heat from a fire, hot plate, exothermic reaction, or friction!

What Happens to Entropy?

What exactly is thermodynamic entropy remains for the world to decide. Possible definitions for entropy include:

a) A measure of how much effort would be required for a system to return to its original state. Since eqn 1.50 is only an approximation for entropy change generated by thermal energy changes, it is hard to gauge how scientific this understanding

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would be.

b) A heat capacity for non-homogeneous systems i.e. Eqn 1.49. Heat capacity could remain for homogenous systems of single state of a single type of matter.

c) Associated with work, hence $PdV = TdS$. Of course this needs some thought as it is really based upon the entropy change within a freely expanding system, which is a concept based upon the illogical association between randomness and energy.

d) As Boltzmann's guise i.e. eqn 1.53. If Boltzmann's entropy remains then Ω should only be a function of the system's energy. Hence the traditional concept that entropy relates to the randomness within an expanding system, is fool's gold at best. In other words the relation between entropy to volume becomes suspect.

e) Atkin's guise that being the quality of energy. As will be seen in this book; the higher a system's pressure is in relation to the surrounding atmosphere, the more work per unit volume that the system can do. Ditto the higher a system's temperature is, the more energy per unit volume that can be extracted from that system.

Entropy can only be any one of the above, or something else or even expunged. It cannot remain something for everything, because without some exacting clarity, it remains meaningless.

Closing Remarks

The traditional insistence of writing thermodynamic around a false postulate (second law) has led to the mathematical contrivance¹⁰ known as entropy, being habitually used although nobody knows what it means. This creates many problematic concerns that few have dared to address with any conviction. Never forget; although empirical data can disprove a theory, it cannot necessarily prove any one theory i.e. more than one given theory can explain given empirical findings. Hopefully even those indoctrinated in the science may actually open their minds to other plausible simpler explanations for our various empirically verified findings. Concepts like Helmholtz free energy will be shown to be right but for the wrong reasons!

In the ensuing chapters, new considerations of the science's fundamentals will be presented. It will be up to the reader to determine whether our new perspective is more palatable what is accepted. It is hoped that you will be open minded, void of indoctrination and abide by the principles of Occam's razor (Ockham's razor), which is paraphrased: "*All things being equal, the simplest solution remains the best*".

Hopefully you will find that the solutions described in this book are simpler than what is currently accepted traditional mainstream. After clearly demonstrating that a simpler constructive logic based explanation exists, some of the problems with entropy and second law based thermodynamics will be revisited in Chapter 16.

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