

Lectures on Thermodynamics.

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Summer 2001

Chapter 1

Energy Accounting, Variables and Properties of Systems

1.1 INTRODUCTION AND DEFINITIONS

The History of Thermodynamics

The subject of thermodynamics has a diverse history. Originally developed in the 18th and early 19th century for understanding how much work steam machines could produce, in the middle part of the 20th century it became the basic framework in which to understand the macroscopic behavior of materials. In some sense thermodynamics may be the eternal subject that has kept its prominent place in science, even when new insights and trends emerge. Now that atomistic and electronic descriptions of materials are becoming more powerful, a new role for thermodynamics emerges as the science that defines the boundary conditions for such microscopic investigations. Even in information theory, probably one of the fastest growing fields of the 21st century, thermodynamics is playing a prominent role in quantifying information content. Definitely Albert Einstein agreed with the prominent role played by Thermodynamics in Science:

A theory is the more impressive the greater the simplicity of its premise, the more different kind of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.

Albert Einstein

Imagine yourself back in the beginning of the 18th century. Newton's understanding of mechanical motion is well penetrated in science and engineering. Robert Boyle has formulated its Law of corresponding states in gasses, but the insight of J.C. Maxwell into electromagnetism is still more than a century away. In 1712 Newcomen builds the first steam-fired engine to lift buckets of water out of mines, one of the biggest engineering problems of that time. The idea of "mechanized power" takes off and propels England into the Industrial Revolution. In the early 19th century, the steam train rolls across the European continent. While it was understood at that time that steam engines essentially convert heat to mechanical work, no quantitative theory was known to predict conversion efficiencies, and heat was not quite yet seen as a form of energy. It is out of the practical engineering need to predict the work produced by steam engines that the science of thermodynamics was born. As is often the case, the engineering moved significantly faster than the science. The formulation of a rigorous framework for thermodynamics only occurred in the mid to late 19th century by people such as Herman Helmholtz, Lord Kelvin, William Rankine, Rudolf Clausius and Willard Gibbs. At that time England had already 10,000 miles of railroad and Union Pacific and Central Pacific had met up to link their trans-continental tracks in Utah so one could now go across the US by train. With so much delay in the development of the core ideas of thermodynamics, let us just hope they are really good.

Why is the subject called thermodynamics ? It is often stated that this is a misnomer because thermodynamics deals with systems at equilibrium (and hence not with the dynamics of how they reach that equilibrium). This interpretation is somewhat misguided and masks the true origin of thermodynamics. In the early 19th century the mathematical description of a mechanical system was quite well known. It was known that forces, equations of motion, etc. could be derived from a function that describes the energy in terms of coordinates*. Thermodynamics came about as the effort to add temperature to the variables that describes a system. In that sense the name thermodynamics (temperature + mechanical dynamics) is actually quite well chosen.

Thermodynamics is what we refer to as a macroscopic science. It does not use or produce any information about the microscopic nature of matter. Materials are simply treated as systems defined by a few properties and equations of state. Because it is blind

* Similar to what we now think of as Hamiltonians or Lagrangians

to what is inside the system, thermodynamics can not independently generate numerical data about a specific system. Rather thermodynamics develops relations between properties of materials, and links together data which may at first glance seem completely unrelated. This is both the strength and weakness of the subject. To get an actual number for the property of a material thermodynamics always requires input, either from an experimental measurement, or as has been the case more recently, from quantum mechanical calculations on materials. Just remember NINO: Nothing in, nothing out. Because the equations of thermodynamics are not system specific, it is almost universally applicable. One of the more satisfying aspects of the subject is that the general equations of thermodynamics apply to any system, whether it is a power plant, a piece of material, or yourself.

1.2 SYSTEM AND SURROUNDINGS

A thermodynamic *system* is a well-defined part of space or matter. It can be defined by a boundary or as a certain piece of matter. The word *system* is therefore used in a much more general sense than you may be used to. The system *boundaries* do not need to be physical boundaries, nor do they need to be localized in space. As an example, let us define as a system, all the water molecules contained in a rain drop. When the drop splatters on the ground, it breaks up in many parts. Some may run off into a creek, while others may evaporate or even combine chemically with other materials (e.g. in a plant). In principle, after the rain drop has hit the ground, our system can still be defined as all the water molecules that were originally in the drop. Of course, in practice it will be very difficult to keep track of such a system. The particular choice of system is often crucial for solving a thermodynamics problem. For the same physical situation a clever system definition can lead to a short elegant solution, while other definitions may only lead you down a path of cumbersome math.

Clearly, the definition of a system is intimately related to the choice of a *boundary*. System boundaries can be *open* or *closed* to matter, rigid or *deformable*, *insulating* or *heat-transparent*. Even more esoteric boundaries may be specified, e.g. a wall that lets A and B through in opposite direction and in the proportion of one A molecule for every two B molecules. As long as it can be fully specified it is an acceptable definition for a system boundary. Just remember that a system can be either defined in terms of a boundary (physical or non-physical) or by "tagging" a certain amount of matter (as in the case of the rain drop). Everything in the universe that is not part of the system will be referred to as the *environment* or the *surroundings*. Hence, the *universe* is everything (system + surroundings).

Usually it is possible to describe the same physical situation with a number of different system definitions. Take for example in figure 1, the heating and evaporation of water from a beaker that is being heated with a gas burner. One may take as the system the beaker of water. In that case, it is an *open system* since matter (the evaporating water) leaves the system. Alternatively, one may take as the system all the water that is initially

in the beaker (even after some of it has evaporated). This will be a *closed system* from which no matter leaves, by definition. An other alternative is to include the gas burner in the system. In this case there is no heat flow into the system (unlike in the first two cases). Obviously, different system definitions should lead to the same physical results, and each choice is a-priori not better than the other. We will later see that the explicit terms in the basic equations of thermodynamics will have a different value for different system definitions. Often a smart choice of for the system definition may therefore make it possible to zero some terms in equations and lead to easier solutions. So remember, the obvious system choice is not always the most convenient one to solve a problem !

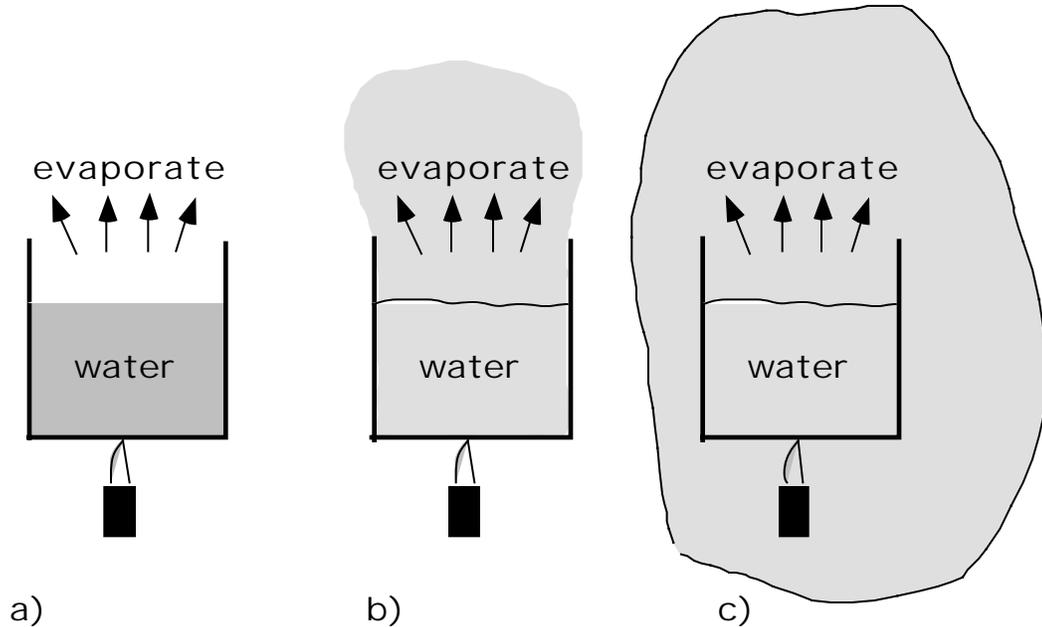


Figure 1.1: Water evaporates from a beaker that is heated with a burner: three different system definitions:

- a) system = liquid water: system is open for matter and energy
- b) system = all water, liquid or vapor: systems is closed for matter
- c) system also includes burner: no heat flow into the system.

1.3 CONSERVATION OF ENERGY: THE FIRST LAW OF THERMODYNAMICS

Conservation principles are quite general in physics. The First Law of Thermodynamics is simply the *conservation of energy*. In words, it states that energy is never destroyed nor created, merely exchanged between different parts of the physical

world¹. In thermodynamics, energy exchanges occur across the boundaries of a system. The First Law implies that the sum of all energy flows across the boundaries of a system is equal to the net change of energy of the system:

$$\sum_{\text{boundary}} \text{energy flow} = \Delta(E_{\text{system}}) \quad (1.1)$$

In this definition, the energy flow is taken to be positive (negative) when it goes into (out of) the system. We use the symbol Δ to denote a finite change of a quantity (as compared to an infinitesimal one). The First Law is like balancing a checkbook. To figure out the balance of your account you start with the old balance, add the deposits and subtract the expenses.

THE UNITS OF ENERGY

Although this conservation principle may seem obvious to you, it was only established around the early to mid 19th century by such scientists as Sadi Carnot^{2*}, Emile Clapeyron and James Joule, names you will hear many more times in this course. One of the difficulties in formulating the First Law was that in order to verify the conservation of energy one needs to be aware of all manifestations of energy flows. Otherwise "magical" energy increases or decreases show up in a system (similar to an anonymous donor in your checking account^{*}). Although the equivalence between mechanical forms of energy was understood in the early 19th century, the quantification of heat as an energy flow was hotly (pun!) debated at the time.

Equation 1.1. already shows the nature of Thermodynamics. To figure out what happens to a system we observe it from the outside (observing what happens across its

¹ At this point you may be distressed about relativity and the fact that energy can be converted to mass and vice-versa. Not to worry. We will only deal with non-relativistic situations in this class. If one day you are going to work on nuclear bombs or perform research on the solar system, you will be happy to know that the First Law has been extended by some to include the energy-mass conversion. In this formulation of the first Law it is simply $E + mc^2$ which is conserved.

² Sadi Carnot also has the distinction of being one of the few generals in Napoleon's army who was never defeated. He must have been absent at Waterloo.

* just you wish

boundary.) Since one can never "measure" the energy of a system, the only way one can keep track of it is by observing how it is modified.

The remainder of this chapter is used to bring equation (1.1) in a form where it is of practical use to us. To get there, we need to find an explicit way to calculate the energy flows (left hand side of equation 1) and say something about the different ways in which a system can store energy (right hand side of the equation.) Being Engineers that should not be all. Ultimately we are not interested in the energy of a system, but in its more relevant properties. We will therefore try to relate changes in the energy to changes in other variables that describe the system. For example, in an electrically heated house, the system's (= house) energy goes up when we draw electrical power from the grid, but what we ultimately are interested in is to figure out what the temperature increase is of the house. So we need to relate the energy of the house to its temperature.

So the scheme is as follows:

observe energy flows -> obtain energy change of system -> relate to property change

1.4 THE ENERGY OF A SYSTEM

When the net energy flow over the boundary of a system is not zero, the system's energy will change. The components of the system's energy related to motion are the kinetic energy (E_{kin}) and the potential energy (E_{pot}). All other sources and sinks of energy of a system are referred to as *internal* energy (E_{int} or U):

$$E_{system} = E_{kin} + E_{pot} + E_{int} \quad (1.2)$$

For a system at rest, the variation of system energy will equal to variation of internal energy:

$$\Delta E_{system} = \Delta E_{int} \equiv \Delta U_{sys} \quad (1.3)$$

In this course we will only deal with systems at rest, so the change of the system energy will always be the change in internal energy.

The concept of *internal energy* is really a thermodynamic invention. If you were to look in detail *into* the system, you would obviously find that that energy goes into kinetic or potential energy of the parts that make up the system. For example, when the energy of a system is raised by heating it, that energy is actually stored in the potential and kinetic energy of the electrons and atoms. But since the thermodynamic laws have to be oblivious to the content of the system, we have to act like we do not know how energy is taken up. Hence we simply call it internal energy of the system and make no judgment

on how energy is stored internally. Clearly, this is in line with our earlier description of thermodynamics as a purely macroscopic science.

1.5 ENERGY FLOWS

The mechanisms by which energy can be exchanged with a system are called *energy flows*. Typically, these are divided into three categories: *heat*, *work* and *matter* flow.

Heat (symbol Q) is the exchange of energy between a hot and a cold body. Work (symbol W) is the result of mechanical, electrical or magnetic action upon on a system. A simple example of work is the mechanical work that is exerted when we push onto a system. The work in this case is the force applied times the displacement*. The action that results in work is not always as visible as in the previous case of mechanical work. For example, when current is drawn from an electrical transformer, the primary coil performs magnetic work on the secondary coil, even though these coils are not in contact with each other.

A system that is open can also exchange energy because of a net flow of matter (symbol M). Since the molecules that flow across the boundary of a system transport energy with them, this flow needs to be accounted for in the energy balance for the system. An example of matter flow is the action that occurs when you drive up to a gas station and fill up the car with gas. The gasoline increases the internal energy of the car. Later this will be converted to kinetic energy of the car.

With these definitions the First Law of Thermodynamics can be written as:

$$Q + W + M = \Delta E_{\text{sys}} \quad (1.4a)$$

The mass flow is often written explicitly as the sum of the contributions from various chemical components i :

$$M = \sum_i m_i \mu_i$$

where μ_i is the energy associated with component i .

Often we will deal with a closed and stationary system so that equation 1.4. reduces to:

$$Q + W = \Delta U_{\text{sys}} \quad (1.5)$$

This is a good time to say something about equations. Thermodynamics has many of them. Trying to remember them without remembering the conditions under which they are valid is useless. Rather than remembering the equations, try to focus on the concepts they reproduce. Equation 1.5. still represents the same concept as equation 1.1., namely that the energy change of a system can be calculated by summing the net energy flow across its boundaries. All we have done in (1.5) is limiting those flows and energy changes to a specific, but common, case.

* More exactly, work is the scalar product of the force vector with the displacement vector

1.6 DIFFERENTIAL FORMULATION OF THE FIRST LAW

In many cases we will look at infinitesimally small parts of a process. Infinitesimal flows are distinguished from infinitesimal changes in the properties of the system by using another differential operator (δ for flows, d for properties). With this convention, the First Law can be written as:

$$\delta W + \delta Q + \sum_i d m_i \underline{\mu}_i = dU_{sys} \quad (1.6)$$

where μ_i is the specific energy of component i (i.e. the energy per kg or per mol, etc.).

1.7 TYPES OF WORK

There are a variety of ways to perform work on a system. All work terms take the form of some generalized force times a response of the system.

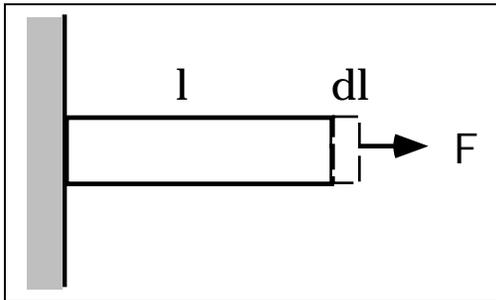
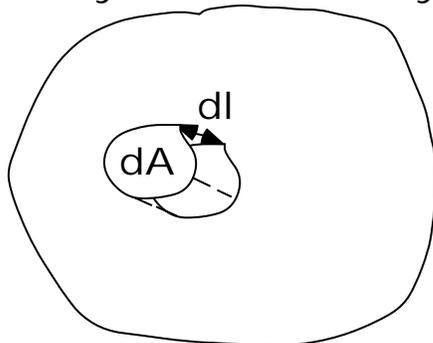


Figure 1.2: Pulling on a bar so that it extends causes energy to flow into the bar.

Mechanical Work

Figure 1.2 shows a system being elongated by the application of a force. The work performed by this force is $F \cdot dl$. This example produces a one-dimensional stress state. In general the mechanical energy transferred to a system by stressing it is

System Boundary



$$\delta W = V \sum_{i,j} \sigma_{ij} d\epsilon_{ij}$$

where σ is the stress and ϵ is the strain.

V is the volume of the system.

One particular case of isotropic stress is a pressure change. If the system's properties are isotropic the above equation can be simplified considerably. The force on an infinitesimal area element of the material is $-pdA$, where A is the area of the system. The work done by extending that area element out an amount dl along the normal of dA is $-p.dA.dl$. It can easily be recognized that $dA.dl$ is the change increase in volume associated the extension of that area of surface. Integrating this over the complete surface gives the common formula for the work performed by volume changes of a material in a pressure field:

$$\delta W = -pdV \quad (1.8)$$

This is the most common mechanical work term for thermodynamic systems and is always effective when a system undergoes changes under constant pressure. It can be interpreted as follows: When a system expands ($dV > 0$) the boundary pushes against the force of the outside pressure. Hence work is performed on the environment and the system loses some energy to the environment. Similarly a shrinking system ($dV < 0$) receives energy from the environment as the pressure performs work on the system.

Electrical Work

Systems can also exchange energy as electrical work. If the system is at potential ϕ with respect to the environment and an infinitesimal amount of charge dq of charge is transferred from the environment to the system, work in the amount of ϕdq is performed on the system by the environment. Hence in this case:

$$\delta W = -\phi dq \quad (1.9)$$

Magnetic Work

Similarly, systems that can be magnetized can receive or perform work in a magnetic field. Think of the force needed to pull a magnet from your refrigerator !. The following field variables are defined in magnetism:

H: applied field

M: magnetization (of the material)

B: induction $B = \mu_0(H + M)$

The work performed in a magnetic field is $H.dB$, which can be rewritten as:

$$\delta W = HdB = \mu_0 HdH + \mu_0 HdM \quad (1.10)$$

The first term ($\mu_0 HdH$) is the work performed on the applied field itself and would be present even without a material there, whereas the second term is the work performed on the material in the field. If we only treat the material as the system, only the term ($\mu_0 HdM$) should be counted. In magnetism work, magnetization is typically

given per unit volume. Hence to account for all the work one needs to multiply with the volume:

$$\delta W = \mu_0 V H dM \quad (1.11)$$

One can encounter more work terms than these in thermodynamics. These will always have the form of $X.dY$, where X is some “force” and Y is a “response” of the material. For example, in electrical work ϕ is the driving force and dq is the resulting displacement of charge. Similarly in magnetism, H is the applied field and M is the resulting magnetization.

These variables X and Y that appear together in a work term are called *conjugate variables*. Hence (p,V) is a conjugate pair. So are (H,M) and (V,q) . Later we will see other conjugate pairs.

1.8 SOME EXAMPLES OF WORK

Spring

Generalized strain

Capacitor

magnetism: the hysteresis loop

1.9 STATE VARIABLES

Previously we wrote down the First Law of Thermodynamics. It basically states that the net balance of energy flows over the boundary of a system changes the energy of the system. A change in energy of a system will modify the system in some way. We will say that it changes the *state* of the system. For example, an increase in kinetic energy of the system will change the velocity of the system. An increase in internal energy may lead to a change in temperature or volume of the system (we will see later that many other properties of the system can change as well). All these variables that characterize the state of a system are called, appropriately, *state variables*.

How many variables, and which ones, are needed is a subtle problem in thermodynamics. Typically, the state variables are Temperature (T) and the variables that appear in the work differentials that can exchange energy with the system. These are the properties of the system that can vary (hence the name “variable”).

Note that state variables do not completely specify a system. Many other features of a system may determine the state functions, even though these features do not change during a typical thermodynamics process. We will call these attributes of the system *parameters*. For example, compare a piece of pure, perfect, crystalline copper with a cold-worked piece of Cu. These are obviously not exactly the same systems as the latter

copper will have a much higher dislocation density. This difference may be relevant when integrating the $F \cdot dl$ term if the two materials differ in elastic properties. Hence, the dislocation density can be treated as a parameter. Chemical nature is essentially also a parameter. For a closed system, the number of moles of each chemical component (assuming no chemical reactivity between the components) is a parameter; for an open system it is a variable.

In the most strict sense, one could argue that every characteristic of a system should be captured either in its state variables or parameters. In practice we often get away with much less and we will neglect these more subtle attributes of materials that modify the thermodynamic properties very little.

The number of variables is not the same as the number of independent degrees of freedom for the system as some variables are related to each other. It can be shown that for each conjugate pair of variables appearing in a work term, there is an *equation of state* that relates them. This equation of state is a property of the system. In other cases there may also be *equilibrium relations* that constrain the variables to certain relations.

Example: Simple ideal gas

A single component ideal gas can be completely characterized with four variables from: *volume, pressure, temperature* and *number of moles*. There is one conjugate work pair (p, V), hence there is one equation of state ($PV = nRT$). Three variables therefore suffice to fully specify the system. If the ideal gas is a closed system, the number of moles is a parameter and the system can be specified with two independent variables.

Extensive and Intensive Variables

Extensive variables scale with the size and amount of system. Hence these include variables such as volume, mass, internal energy ... *Intensive* variables are size independent and include variables such as temperature, pressure, electrical potential. *Densities* are extensive variables that are normalized by another extensive variable (usually the size or mass of the system). These include concentration (which is some number of moles divided by another number of moles or divided by the volume), specific volume, magnetization density (M) etc.

1.10 THE SIMPLE SYSTEM

A *simple* or *limp* system is the most basic system of thermodynamics. It can be described with only p, V, T . Hence it only has one work term ($-pdV$) and one equation of state. Its state is fully characterized whenever two variables are specified. Note that a *simple* system has to be isotropic in its properties, otherwise the mechanical work term would be more complicated than $-pdV$. Many closed systems of liquids or gasses can be approximated as *simple*. The approximation is also used often for solids when no

mechanical stresses (besides pressure fields) are present. Obviously no magnetic or electrical work flows can be present in a *simple* system.

1.11 STATE FUNCTIONS

As their name implies, *state functions* are functions of the state of the material and only of the state of the material. Most properties you know are state functions, meaning that they always have the same value when the material is in the same state, regardless of how it got there or how long it has been there. You can think of state functions as functions of the state variables.

Example:

The internal energy of an ideal gas is a function of only three variables:

$$U_{\text{ideal gas}} = U(T, p, n), \quad (1.12)$$

or

$$U_{\text{ideal gas}} = U(T, V, n), \quad (1.13)$$

or any other three variables from p, V, T, n .

If the system were closed, n would be a parameter and one could write $U_n(T, P)$, though usually the subscript n is not written.

1.12 DIFFERENTIALS

We will never really have an explicit form for a state function such as the energy in terms of the state variables. Actually, if you came up with an exact form of a state function for a real material, I would place my bet on you for a Nobel Prize in a few years. Fortunately, we can get by with less information. Most often we will not be interested in the absolute value of a state function, but in the difference between two states. This difference can be computed with our favorite tool: differential calculus. Let's do this very formally at first and then go through some examples. If the internal energy of a system depends on a bunch of state variables X_i with i going from 1 to N , then any infinitesimal change in U , caused by an infinitesimal variation of the state variables can be computed from the total differential of U :

$$\begin{aligned}
 dU &= U(x_1 + dx_1, x_2 + dx_2, \dots, x_N + dx_N) - U(x_1, x_2, \dots, x_N) \\
 &= \left(\frac{\partial U}{\partial x_1} \right)_{x_2, x_3, \dots, x_N} dx_1 + \left(\frac{\partial U}{\partial x_2} \right)_{x_1, x_3, \dots, x_N} dx_2 + \dots + \left(\frac{\partial U}{\partial x_N} \right)_{x_1, x_2, \dots, x_{N-1}} dx_N \quad (1.13)
 \end{aligned}$$

If we need the internal energy change between two states, 1 and 2, that are more than an infinitesimal amount away, we will of course have to integrate this equation between state 1 and 2. Again, the reason we have to do things this way is because we will never really know the function U . You will see later, however, that the partial derivatives of U with respect to the state variables are things we can often measure. So we don't know the function, but at least (sometimes) we will know the derivatives.

Also note that if the two states for which we need the internal energy difference have the same value for some state variable X_i , its differential, dX_i , is zero in equation (1.13) and we don't need to know the partial derivative of U with respect to that variable*. Yes, more stuff we don't need to know !

Anything stated here for the internal energy U is applicable to all other state functions as well.

1.13 INTEGRATING DIFFERENTIAL EQUATIONS

If we need to compute a change in a quantity between states we can integrate the differential equation that describes its change. For example, let's assume we need to know the internal energy difference between two states that only differ in the value of X_1 and all other variables have the same value in both states. We can obtain this internal energy difference by integrating equation (1.13):

$$\int_{state\ 1}^{state\ 2} dU = \int_{state\ 1}^{state\ 2} \left(\frac{\partial U}{\partial x_1} \right)_{x_2, x_3, \dots, x_N} dx_1 = \int_{state\ 1}^{state\ 2} F dx_1 = U(state\ 2) - U(state\ 1) \quad (1.14)$$

Not every infinitesimal quantity is the differential of a function. For example, the work in a simple system is the integral of $\delta W = -pdV$. Since the state of a simple system can be specified with two variables, we can plot the changes of such a system in a two-dimensional p - V diagram (figure 1.4). In this diagram, the total work done in going between two states is minus the integral under the curve describing the trajectory between the two states. Clearly, the work performed along trajectory I is larger than along trajectory II(a+b). The reason for this difference is that δW is not the differential of a state function (property). W is an energy flow and there is no function $W(X_1, X_2, \dots)$,

* Of course, this is not completely correct. The partial derivatives are themselves state functions and, in principle, they also depend on *all* the state variables. Though luck !

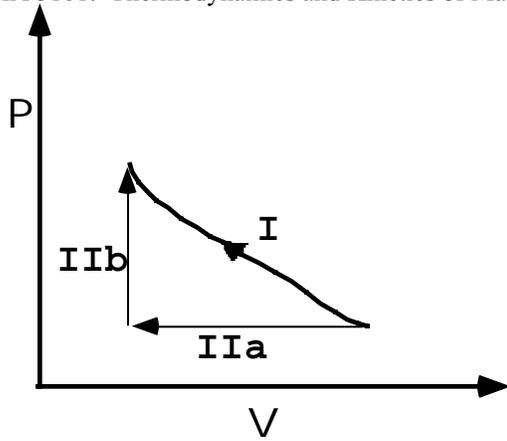


Figure 1.4: Work performed depends on path between states

X_N). The integral of δW is path-dependent, whereas the integral of the differential of a state function ($=$ property) is not path dependent.

Note that since the First Law for a simple, closed system gives $dU = \delta W + \delta Q$, the integral of δQ is necessarily also path dependent (since the integral of dU is NOT path dependent).

1.14 OTHER PROPERTIES

Some other properties of systems often appear in thermodynamic equations.

Heat capacity

The heat capacity is defined as the ratio of the heat input to a system to the temperature change induced:

$$C = \left(\frac{\delta Q}{dT} \right) \quad (1.15)$$

The above equation does not yet fully specify a unique value of the heat capacity since δQ depends on the path taken (Remember, it is not an exact differential?). Since a simple system is described by two independent variables, specifying a dT is not sufficient to describe the path taken. Hence, more correctly, equation (1.15) should look like:

$$C_{\text{path taken}} = \left(\frac{\delta Q}{dT} \right)_{\text{path taken}} \quad (1.16)$$

For simple systems the path can be specified by indicating what occurs to one of the other variables (e.g. p or V). The most common heat capacities used are the constant pressure heat capacity and the constant volume heat capacity:

$$C_p = \left(\frac{\delta Q}{dT} \right)_p \quad (1.17)$$

$$C_v = \left(\frac{\delta Q}{dT} \right)_v \quad (1.18)$$

Note that the right hand sides are not partial derivatives (since Q is not a *function*), but simple the ratio of two infinitesimal quantities. Most often we deal with the heat capacity that is normalized per unit mass of the system. Per mole, equations (1.17-18) become:

$$c_p = \frac{1}{n} \left(\frac{\delta Q}{dT} \right)_p \quad (1.19)$$

$$c_v = \frac{1}{n} \left(\frac{\delta Q}{dT} \right)_v \quad (1.20)$$

Note that in principal, one could specify plenty of other heat capacities along more complex paths. These heat capacities would be some combination of the properties defined under constant V and p . In the case of systems that need to be described with more than two variables, there will be more than two heat capacities (e.g. a system with magnetic or electrical fields).

Values of heat capacities

C_p for air $\approx 30 - 33$ J/mol-K

C_p for water ≈ 75 J/mol-K = 1 kcal/kg-K

C_p for iron ≈ 24 J/mol-K

Heat capacities are temperature dependent.

For gasses a rule of thumb is that for monoatomic gasses (Ar, Kr, ...):

$C_v \approx 3/2 R$ and $C_p \approx 5/2 R$

For diatomic gasses (O_2 , N_2 , ...):

$C_v \approx 5/2 R$ and $C_p \approx 7/2 R$

Exercise

Write down the possible heat capacities for a system in a magnetic field ?

Thermal expansion:

Linear thermal expansion is defined as the relative change of length per unit temperature at constant pressure:

$$\alpha_l = \frac{1}{l} \left(\frac{dl}{dT} \right)_p \quad (1.21)$$

Because we often deal with shapeless system, it is more convenient in thermodynamics to use the volumetric thermal expansion:

$$\alpha_v = \frac{1}{V} \left(\frac{dV}{dT} \right)_p \quad (1.22)$$

It can be easily be shown that $\alpha_v = 3 \alpha_l$.

VALUES OF THERMAL EXPANSION

Compressibility

Compressibility is defined as the relative change of volume with pressure at constant temperature:

$$\beta_v = -\frac{1}{V} \left(\frac{dV}{dp} \right)_T \quad (1.23)$$

The minus sign is used to make the compressibility positive (since volume decreases with pressure). Note that compressibility is the “volume version” of elastic constants for solids.

Sometimes an *adiabatic compressibility* is also defined.

1.15 SOME PROPERTIES OF IDEAL GASSES

An *ideal gas* is a particular substance that has a very simple equation of state. Many real gasses behave as ideal gasses when they are well above their condensation temperatures. From the ideal gas equation several other relations can be derived. When you use these relations, always keep in mind that they only apply to ideal gasses. Hence the equations derived from them will not be generally applicable to all materials.

Properties of ideal gasses:

I: $PV = nRT$

II: $c_p - c_v = R$

III: $\left(\frac{\partial U}{\partial V}\right)_T = 0$

Property III implies that the internal energy of a closed ideal gas only depends on its temperature. It is left for the reader to prove that:

$$dU = nc_v dT \quad (1.24)$$

So that the internal energy only depends on temperature. Please keep in mind that this is only true for an ideal gas. For other systems, the internal energy will also be a function of other state variables (and often strongly so).

1.16 EXAMPLES

- 1) Calculate work during isothermal compression of an ideal gas
- 2) Adiabatic compression + applications

1.17 THE ENTHALPY

Many practical processes occur under constant pressure. Under this condition, a system can always perform or receive energy through a change in volume (pdV term). This becomes relevant when we consider for example the heating of a material. The internal energy of a material determines its temperature. Say I could figure out how much internal energy I need to add to raise the temperature of a system by one degree. One might think that if I add that amount of energy by supplying heat a one-degree temperature rise would occur. This is not correct. If some amount of heat flow raises the temperature of a material, its volume will also change (usually expands). This expansion causes work to be performed on the environment through the pdV term. Clearly, some of the energy we put in as heat directly leaves the system again as work on the environment ! Hence not all the heat we put is used to raise the internal energy. For this process we can write:

$$dU = \delta Q - pdV \quad (1.25)$$

The change in internal energy is the net balance of the heat flow in and the work performed on the environment from the expanding system. The amount of heat I need to supply to obtain my internal energy increase is actually:

$$\delta Q = dU + pdV = d(U + pV) \quad (1.26)$$

The latter equality is true because we only consider constant pressure changes. Because it so often occurs in thermodynamics, the combination $U + pV$ is given a new name, the *enthalpy (H)*. Enthalpy is defined as:

$$H \equiv U + pV \quad (1.27)$$

For a simple system the enthalpy change of the system in a process under constant pressure is the amount of heat added to the system:

$$(dH)_p = (\delta Q)_p \quad (1.28)$$

Again, note the restrictions on this equation. It is only true for a simple system (with only pdV work) and under constant pressure.

The enthalpy finds much use in studying chemical reactions:

For example, if one wants to find the total heat released (or absorbed) in the isothermal, isobaric reaction



one only needs to calculate the change in enthalpy in going from the reactants to the product(s). If the reaction occurs at 298K, the heat exchange is:

$$Q = H_{CO_2}^{298} - H_{CO}^{298} - \frac{1}{2} H_{O_2}^{298} \quad (1.29)$$

Enthalpies of most compounds are tabulated at 298K (or other temperatures). Since as with energy, the enthalpy has not absolute zero, a reference state has to be agreed on. For the elements the state of zero enthalpy is taken as the stable form at 298K and 1 atm pressure. Hence for oxygen, this is molecular oxygen in a gas; for carbon it is graphite. Once the enthalpy of elements is set, the enthalpy of compounds is determined by the heat release in their isothermal, isobaric formation reaction. This *enthalpy of formation* is often tabulated at 298K and can be taken as the value of the enthalpy for that compound at 298K.

1.18 TEMPERATURE DEPENDENCE OF THE ENTHALPY OF MATERIALS.

While the enthalpy of materials is tabulated at 298K, the enthalpy at other temperatures can be found from the relation between the heat flow and the enthalpy:

$$dH_p = \delta Q_p = n c_p dT \quad (1.30)$$

Hence,

$$c_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (1.31)$$

In a material the specific enthalpy increases with temperature proportional to the heat capacity. At a phase transition, the enthalpy varies by a discontinuous amount which is equal to the latent heat of transformation. For example, the heat required to melt ice at 0°C is equal to the enthalpy difference between the liquid at 0°C and the ice at 0°C. Figure 1.5 shows a typical evolution of enthalpy with temperature.

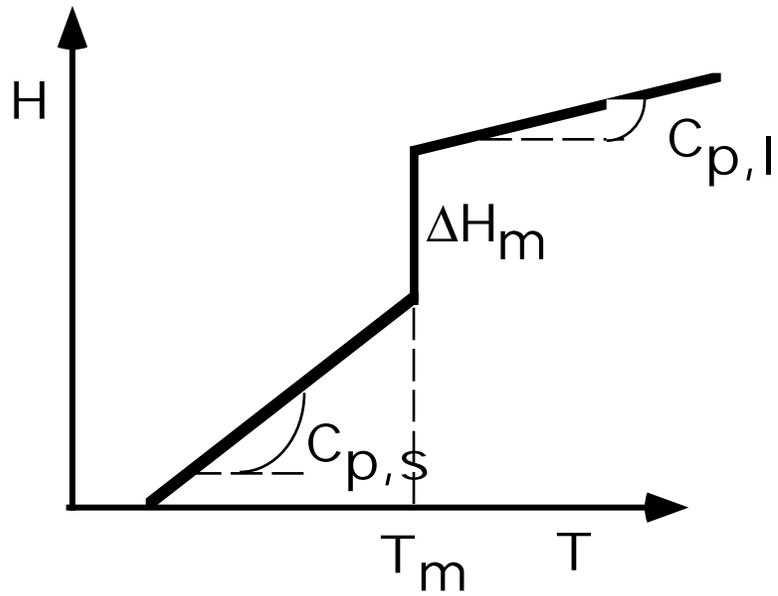


Figure 1.5: Enthalpy as function of temperature. At a transition the enthalpy is discontinuous.