

Principles of Energy Conversion

Part 6. Review of Engineering Thermodynamic

February 7, 2018

12 From Atmospheric Engines to Thermodynamics	3
12.1 Work from Steam	4
12.1.1 Measuring Pressure and Volume - Engine Indicators	5
12.1.2 Modern Engines	5
12.1.3 Boundary Motion Work & Polytopic Processes	6
12.2 Steam from Heat	7
12.2.1 What is heat?	7
12.3 Heat and Work on an Atmospheric Engines	8
12.4 Forward to Engineering Thermodynamics	9
13 Engineering Thermodynamics	11
13.1 What is Thermodynamics?	12
13.2 Accumulation of Thermal Energy	14
13.3 Accumulation of Mechanical Energy	15
13.3.1 Gravitational Potential Energy	15
13.3.2 Kinetic Energy	16
13.3.3 Elastic-Strain Energy	17
13.3.4 Flow Potential	18
13.3.5 Magnetic Potential	20
13.4 First Law of Thermodynamics	20
13.5 Enthalpy	21
13.6 Rate of Energy Change	22
13.6.1 Useful Simplification to Rate Equation	23
13.7 Measurable Properties and Changes in Energy	24
13.7.1 Specific Heats (c , c_v , c_p)	25
13.7.2 Changes in Enthalpy	26
13.7.3 Specific Heats for an Ideal Gas	26
13.7.4 Specific Heat for Liquids and Solids	26
13.8 State Property Relationships	27
References	30

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Article 12

From Atmospheric Engines to Thermodynamics

Figure 12.1 illustrate the basic components and development of early atmospheric engines. As the development proceeded, engineers looked for ways to improve performance (power and efficiency) and for methods of measuring performance. These engines, however, preceded the formulation of the first and second laws. The effort to improve engine performance and improve the understanding of the interaction between heat and work led to the formulation of thermodynamic laws and the development of modern engineering thermodynamics.

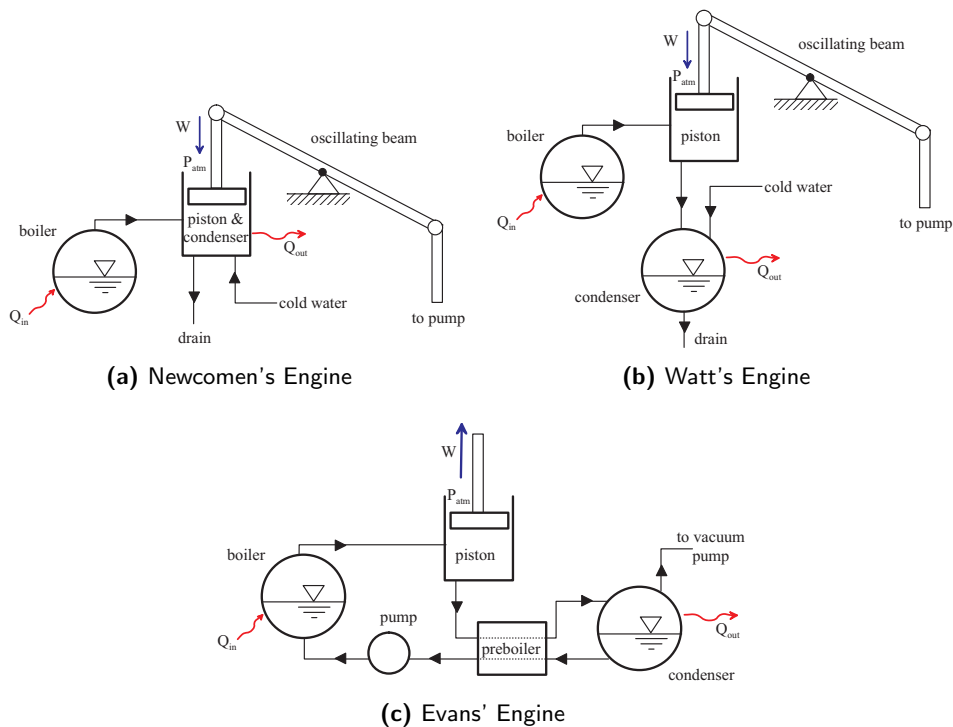
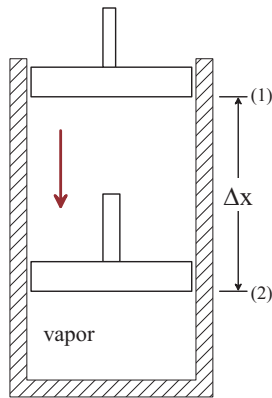


Figure 12.1. Development of Early Atmospheric Engines

12.1 Work from Steam



Work is the expansion (or contraction) of a pressurized gas or vapor. From the perspective of a steam cylinder, work is related to pressure P and volume \forall .

$$\text{Work} = F\Delta x = (P_{\text{net}} A_{\text{piston}}) \left(\frac{\Delta \forall}{A_{\text{piston}}} \right) = P_{\text{net}} \Delta \forall$$

P_{net} is the net pressure difference across the piston. For the atmospheric engines, the pressure difference across the slow moving cylinders was equal to $P_{\text{atmospheric}} - P_{\text{saturation}}$, where $P_{\text{saturation}}$ is the pressure at which the steam condenses or evaporates. During condensation, the temperature and pressure of the steam remains constant, but the volume decreases by two or three orders of magnitude. The pressure difference

between the steam and the atmosphere across the piston is constant, so this type of work is referred to a constant pressure process (*isobaric* process).

$$\begin{aligned} \text{Work} &= (P_{\text{atm}} - P_{\text{sat}}) \Delta \forall \\ &= (P_{\text{atm}} - P_{\text{sat}}) A_{\text{piston}} \Delta x \end{aligned}$$

The work extracted from the atmosphere could be measured if the force F exerted by the piston and the piston displacement Δx could be measured during the *power stroke*.

After Evan's engine development, the work was also extracted from pressurized steam and not just the atmosphere. In this work process the pressure difference, $P_{\text{steam}} - P_{\text{atm}}$ may not remain constant during the power stroke. Therefore, the total work during a power stroke requires integration of the pressure and volume.

$$W = \int_1^2 P_{\text{net}} d\forall$$

As engine technology improved and the speed of engines increased, it was not possible to manually record pressure (via a gauge or manometer) and piston position. Some sort of device was needed to quickly measure pressure and volume simultaneously. In 1792, Davies Gilbert proposed a theory for making these measurements, which is known as an engine indicator. In 1796, John Southern, an associate of Watt, invents the engine indicator. [?]

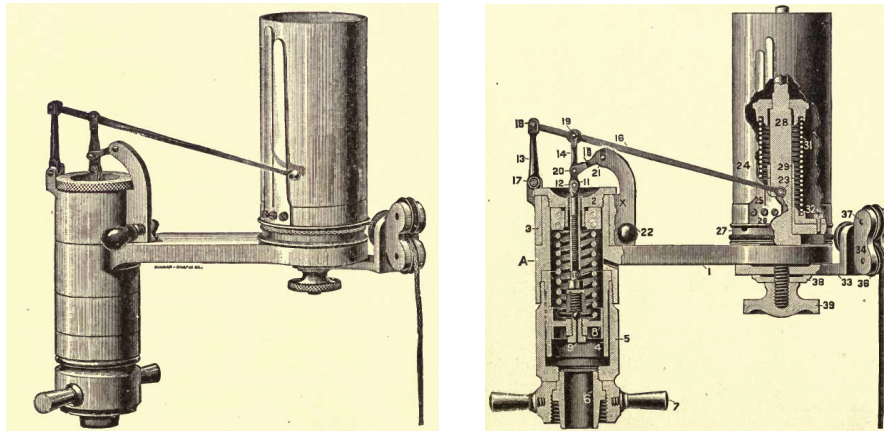


Figure 12.2. Steam engine indicators. [1]

12.1.1 Measuring Pressure and Volume - Engine Indicators

An indicator plot is a pressure-volume plot with pressure on the vertical axis and volume on the horizontal axis. The work is found by integrating over the area swept by the indicator.

$$W = \int Pdv$$

The procedure was to measure height, P , of thin, dV , vertical bands and sum lengths. The proper scaling had to be applied to convert the indicatal lengths to pressure and volume.

12.1.2 Modern Engines

Steam engine indicators are only suitable for low-rpm engines because of the inertia of the indicator components, such as the oscillating drum. As the engine runs faster, the indicator does not accurately reflect pressure and volume in the cylinder. Today, we use crank angle sensors and dynamic pressure transducers to measure pressure and volume. The sensor signals are captured via high speed data acquisition hardware.

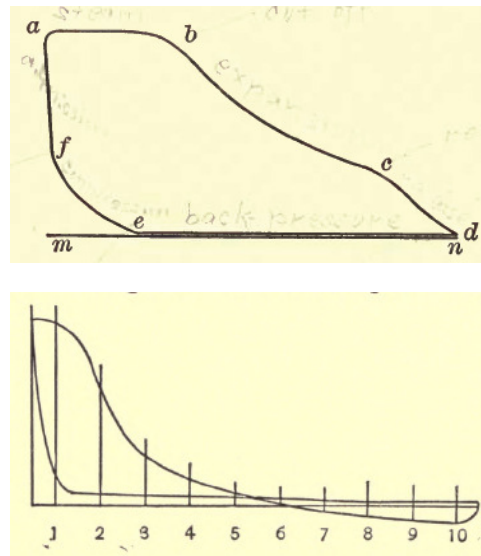


Figure 12.3. Indicator traces. The bottom trace indicates that the steam pressure is than the back pressure from 6 to 10. [1]

12.1.3 Boundary Motion Work & Polytropic Processes

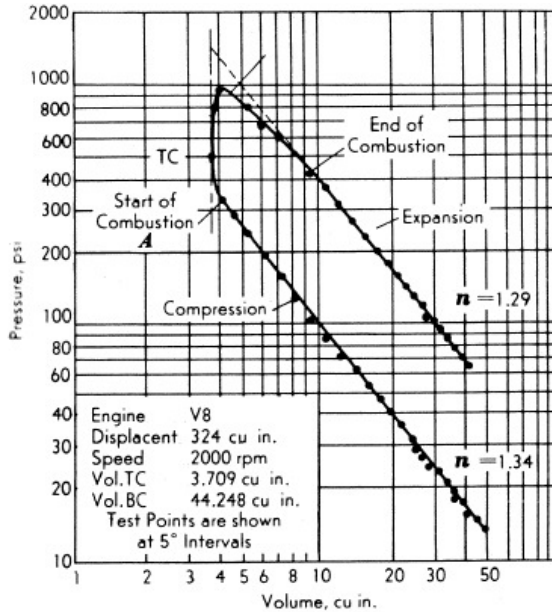


Figure 12.4. Typical pressure-volume trace for an Otto cycle; spark-ignition internal combustion engine. [2]

Engineers found that when the pressure-volume traces were re-plotted on log-log axis, that the power and compression strokes were linear. The power and compression strokes being the portion of the pressure-volume trace which represented work applied to or extracted from the steam. Fitting a linear relationship to the data:

$$\log P = -n \log V + b$$

This relationship can be rearranged.

$$P V^n = e^b$$

where e^b is a constant. Work processes that fit this form are known as polytropic work. The value of the polytropic coefficient n is the slope on a log-log plot, and the slope is a measure of efficiency. For $P V^n = \text{constant}$, integration between V_1 and V_2 provides an analytical expression for work based on the starting and ending states of the steam.

$$n \neq 1, \quad {}_1W_2 = \frac{P_2 V_2 - P_1 V_1}{1 - n}$$

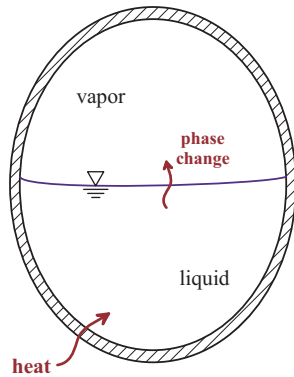
$$n = 1, \quad {}_1W_2 = P_1 V_1 \ln \left(\frac{V_2}{V_1} \right)$$

Four polytropic processes and were these might occur in an atmospheric engine are shown in Table 12.1.

Table 12.1. Polytropic processes and corresponding work.

constant process	polytropic coefficient	polytropic work	atmospheric engine
pressure (isobaric)	0	$P(V_2 - V_1)$	condensing piston
volume (isochoric)	∞	0	closed boiler
temperature (isothermal)	1	$P_1 V_1 \ln(V_2/V_1)$	flow-through boiler
entropy (isentropic)	$\gamma \equiv c_p/c_v$	$(P_2 V_2 - P_1 V_1)/(\gamma - 1)$	ideal piston

12.2 Steam from Heat



The change in the state of steam (water versus vapor) was considered different than that which occurred during the work on the piston. Prior to around 1850, the concept of energy and the relationship between heat and work was not established.

$$\{\text{Heat}\} = \{\text{Change in Steam Energy}\}$$

There were competing theories on how heat transformed water into steam. One of these theories required conservation of heat (as opposed to conservation of energy) and that heat was an independent agent with respect to work. The second theory required that heat and work be interrelated.

12.2.1 What is heat?

Up until the mid-1800's, the relationship between heat, work, and energy exchange with a fluid (steam or gas) was not understood. Work was known to be related to pressure and volume, but how heat was transferred to the steam (or any mass) was a mystery. Two theories were originally put forth to explain heat.

1. **Live Force:** Also known as the *Dynamical Theory of Heat*: Heat is a level of randomness of atoms and molecules in a substance; heat is a form of kinetic energy of very small particles. In other words, heat is manifestation of motion at the molecular level. If work is applied to something, heat can be generated through friction.
2. **Caloric:** Heat is a fluid-like substance that is massless, colorless, odorless, and tasteless. Caloric was a substance that had to be conserved; as such, an important principle of caloric theory is that work can not be converted into heat because work is not a substance.

Caloric theory was proposed by French chemist Antoine Lavoisier in 1789 and was the prevailing theory until the mid-1800's. Caloric is a substance and can be "poured" from one body to another. Since it is a substance, caloric is subject to conservation laws; i.e., caloric is conserved. When caloric is added to a body, the temperature of that body increases. Remove caloric and the body's temperature decreases. When water could no longer contain any more heat, similar to when water can no longer contain any more salt in solution, the water was said to be saturated with caloric. Any additional caloric causes the water to change to vapor (boil). This theory has colored the language of thermodynamics, where we still use the terms *saturated liquid*, *saturated vapor*, and *heat flow*.

Caloric theory was the accepted scientific explanation of how heat is transferred from one mass to another. The theory worked well to explain experimental observations

Article 12 From Atmospheric Engines to Thermodynamics

related to gases and combustion. But caloric theory could not explain observations made by engineers, who routinely put forth the *live force* theory to explain observations during manufacturing.

American Engineer Benjamin Thompson (Count Rumford, 1754–1814) attempted to measure the equivalence between heat and work, a relationship that is excluded in caloric theory. He observed during boring of cannons that heating was continuous due to friction and that heat was not being conserved. There were many others that agreed, such as Black and Mayer, but the science community remained unconvinced.

James Prescott Joule (1818–1889) published experimental results in 1850 [3] that definitively demonstrated that heat is not a substance subject to laws of conservation. Joule was interested in the scaling factor that related units of heat and work and devised an apparatus in which he could measure the work input to a bath of liquid. A falling weight is used to spin a paddle wheel inside a closed, insulated tank of water. He repeated this experiment with mercury. He also repeated this experiment with friction applied to cast iron. His paper concluded with two statements:

1. The quantity of heat produced by friction, solid or liquid, is always proportional to the quantity of force exerted.
2. The quantity of force required to raise the temperature of 1 pound of water by 1 degree Fahrenheit is equivalent to 772 pounds falling 1 foot.¹

Despite Joule's careful experiments, many in the scientific community remained unconvinced and continued to advocate caloric theory for another 50 years.

12.3 Heat and Work on an Atmospheric Engines

Applying the concept that there exists an equivalence between heat and work to the heat engines available led to the mathematical description

$$J \sum_{\text{cycle}} Q = \sum_{\text{cycle}} W$$

where J is the mechanical equivalent of heat, 778.16 Btu/ft-lbf, and the heat and work in and out of the engine are summed over one complete engine cycle. For the atmospheric steam engine this represented one cycle of the piston from top-to-bottom and the back to the top of the cylinder. The total work extracted from the steam during one cycle is the integral over the pressure-volume indicator trace (see §12.1.1).

$$\text{work} = \oint \delta W = \oint P dV$$

where \oint is the integral over the cycle. The symbol δ indicates that the differential is inexact, it does not depend only upon the end points of the integral. In other words, two seemingly identical engines may not have the same work output over a cycle due

¹This measure of heat, raising the temperature of 1 pound of water by 1 degree Fahrenheit (from 63 to 64 °F), was by 1865 known as a British thermal unit (Btu). Today there are four definitions of a Btu (similar to multiple definitions of a calorie) [4]. The current mechanical equivalent of heat is 778.16 ft-lbf per Btu.

to differences in efficiency. The balance between total heat transfer (in and out of the engine) and the total work can be expressed as:

$$J \oint \delta Q = \oint \delta W \quad - \text{ or } - \quad \oint (J\delta Q - \delta W) = 0 \quad (12.1)$$

In the modern context, J is no longer necessary as an indicator of the equivalence of heat and work. It is simply a conversion factor; equal to $1 \text{ kJ}_m/\text{kJ}_{th}$ in SI units. As such, we will not explicitly include the mechanical equivalent of heat J in the energy balances.

12.4 Forward to Engineering Thermodynamics

Joule's experiment provided a mathematical connection between heat and work, which in turn led to the first formulation of the First Law of Thermodynamics for an atmospheric engine (equation 12.1).² The balance between heat and work also holds for each component of the engine,

$$\underbrace{Q}_{\text{heat}} - \underbrace{W}_{\text{work}} = \underbrace{\Delta U}_{\text{internal energy}}$$

where a distinction is now made between heat transmission (heat) and heat storage (internal energy).³ By 1850, *energy* is now being used to describe agents of change that include heat, work, electricity, and magnetism. These agents of change can be transformed, but the total summation of these agents are now considered⁴ to be constant; total energy is conserved.

Using the First Law of Thermodynamics requires a distinction between *system*, *boundary*, and *surroundings*. *System* is the mass of interest. In Joule's experiment the system was the water, which was being stirred and subsequently heated by work transmitted across a *boundary* from an action occurring in the *surroundings*, the falling weight. When the First Law of Thermodynamics is applied, it is always to a system with an identifiable boundary. Energy changes within a system are *stored energy* and energy changes between the system and surroundings (crossing the boundary) are *transitional energy*.

Once established, the concept of energy being conservative and the conceptual difference between system and surroundings catalyzed rapid development of engineering thermodynamics. The utility of engineering thermodynamics is:

1. predicting conversion of heat into work,
2. predicting cyclic conversion of heat into work (heat engines),
3. measuring of energy change, and
4. determining the efficiency of energy change.

In pursuit of these, entropy is introduced and the formulation of the Second and Third Laws of Thermodynamics are finalized.

²The first *Thermodynamics* textbook was published in 1859 by William Rankine. [5]

³The term internal energy, coined by Clausius and Rankine, replaced terms such as inner work, internal work, and intrinsic energy.

⁴except by those adhering to caloric theory

Article 13

Engineering Thermodynamics

Reiterating the last article, engineering thermodynamics is focused on a few key items:

1. predicting conversion of heat into work,
2. predicting cyclic conversion of heat into work (heat engines),
3. measurement of energy change (typically of some fluid), and
4. determining the efficiency of energy change.

These require the use of several abstract concepts, the first of which is energy. Energy cannot be measured directly. We can measure the change in energy only through relating that change to a process. In the case of engineering thermodynamics such processes will involve heat or work.

Using the results from Joule's experiments on the mechanical equivalent of heat, we derive conservation of energy for a process as opposed to cyclic operation of an engine as expressed in equation 12.1.

$$\underbrace{\underbrace{Q}_{\text{heat}} - \underbrace{W}_{\text{work}}}_{\text{transitional}} = \underbrace{\Delta U}_{\text{internal energy}}_{\text{stored}}$$

Here ΔU is the change in *internal energy* between the original *state* of the *system* and the system state after application of heat or work across the boundary as shown in Figure 13.1. An increase in internal energy U represents an accumulation of thermal energy in the system of interest. This is a stored form of thermal energy whereas heat is a transitional form of thermal energy. Heat is energy transference between system and surroundings. As such, it can only be measured or realized at a boundary.

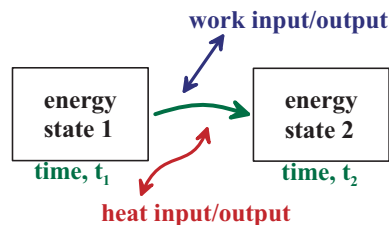


Figure 13.1. Abstraction of First Law of Thermodynamics applied to a system. The application of work or heat across the system boundary is balanced by a change of stored energy.

This balance between transitional and stored energies begs the question of "How do we measure a change in internal energy?". After all, energy is an abstract concept. How do we measure an abstract concept?

13.1 What is Thermodynamics?

“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it you know you don’t understand, but by that time you are so used to the subject, it doesn’t bother you any more.”

– Arnold Sommerfield

“**Thermodynamics**” was first used in a publication by Lord Kelvin in 1849 and the first thermodynamics textbook was published in 1869 by William Rankine. [5] The word thermodynamics comes from the Greek language:

$$\left. \begin{array}{l} \text{therme} \equiv \text{heat} \\ \text{dynamis} \equiv \text{power} \end{array} \right\} \text{“power of heat”}$$

These facts, however, do not help explain what is meant by thermodynamics. A sampling of definitions is provided in Table 13.1. What can be observed from this table is that thermodynamics is a science or maybe a branch of physics or engineering and it involves energy, heat, work, temperature, equilibrium, entropy, transformation of energy, and so much more.

This wide range of applications causes difficulties in how thermodynamics should be organized and taught. This is not a new problem.

“In lecturing on any subject, it seems to be the natural course to begin with a clear explanation of the nature, purpose, and scope of the subject. But in answer to the question ‘what is thermo-dynamics?’ I feel tempted to reply ‘It is a very difficult subject, nearly, if not quite, unfit for a lecture.’”

– Osborn Reynolds

On the General Theory of Thermo-dynamics,
November, 1883

Fundamentally, engineering thermodynamics has been built upon empirical observations. The laws of thermodynamics (1st, 2nd, and 0th) are observations and called “laws” because counter examples have never been observed.

13.1 What is Thermodynamics?

Table 13.1. Common Definitions – Thermodynamics is:

- the science of energy. [6]
- the science of energy and entropy.
- the science that deals with the relationship between heat and mechanical energy and the conversion of one into the other. [7]
- the science that deals with heat and work and those properties of substances that bear a relationship to heat and work. [8]
- the science of the relationship between heat, work, temperature, and energy. *Encyclopedia Britannica, 2018*
- the science concerned with the relations between heat and mechanical energy or work, and the conversion of one into the other. *dictionary.com, Feb. 2018*
- describes natural processes in which changes in temperature play an important part ... in transformation of energy from one form to another. [9]
- an axiomatic science concerned with the transformation of energy from one form to another. [10]
- a branch of physics concerned with heat and temperature and their relation to other forms of energy and work. *Wikipedia, Feb. 2018*
- a branch of physics which deals with the energy and work of a system; only concerned with large scale observations. *NASA K-12 web page, Feb. 2018*
- involves storage, transfer, and transformation of energy. [11]
- the only science that provides a quantitative measure of irreversible processes. [12]
- both a branch of science and an engineering specialty. [13]

13.2 Accumulation of Thermal Energy

Internal energy¹ as a concept is somewhat intuitive. As an object or fluid heats up, there is more intrinsic energy in that object or fluid. Yet quantifying that energy is a challenge. Since energy is not directly measurable, how do we quantify how much thermal energy is being accumulated?

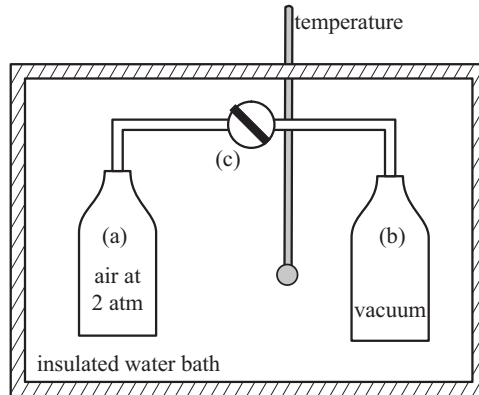


Figure 13.2. Joule's experiment on internal energy change in air.

Joule determined that for gases the internal energy only depends upon temperature.² This determination was based on a simple experiment, illustrated in Figure 13.2, in which air is confined to one of two vessels in an insulated water bath. The vessels were left in the water bath for a long time so that the system (the air) was at a constant temperature (isothermal) and in thermal equilibrium with the surroundings (water bath and the rest of the room). The vessels were connected, but isolated from one another by a stopcock (c). One vessel (a) was filled with air at 2 atmospheres and the second vessel (b) was under vacuum. This is state (1) of the system.

Joule then opened the stopcock allowing the air to move from vessel (a) into the vessel (b) until the pressure equilibrated at 1 atmosphere. This is state (2) of the system. During the change in state of the system (the gas), the water bath did not change temperature. This implies that the system (the gas) also did not change temperature.³ Therefore there was no heat transfer between the system and surrounding; ${}_1Q_2 = 0$. Though the pressure and volume of the system changed, no work was transferred to or from the system; ${}_1W_2 = 0$. Conservation of energy in this experiment becomes:

$${}_1Q_2 - {}_1W_2 = 0 = U_2 - U_1 \quad - \text{ or } - \quad U_2 = U_1$$

¹The term internal energy, coined by Clausius and Rankine, replaced terms such as inner work, internal work, and intrinsic energy.

²More precisely, for ideal gases.

³This implied equivalence is the basis of the Zeroth Law of Thermodynamics. If the system (air) and surroundings (water bath) are at thermal equilibrium and the temperature sensor is at equilibrium with the surroundings, then the temperature sensor is also at equilibrium with the system. On this basis, Joule can conclude that the temperature of the gas did not change when he opened the stopcock even though he measured the temperature of the water bath.

13.3 Accumulation of Mechanical Energy

Since pressure and volume changed and the temperature did not, Joule's conclusion was that internal energy (for air) is only dependent upon temperature.

- internal energy -- internal motion that is disorganized and non-directional; abstract notion of internal energy
- behavior of steam - subcooled liquid, superheated vapor, saturation, critical point, triple point
- sensible vs latent heat
- steam tables & linear interpolation

13.3 Accumulation of Mechanical Energy

There are at least 5 forms of mechanical energy that can be stored; gravitational potential, kinetic, elastic-strain, flow potential and magnetic. These energies may be accumulated in a *system* by application of work, or heat, or both.

13.3.1 Gravitational Potential Energy

For a stationary mass, say a load suspended by a construction crane, the force holding the mass is equal to the weight of the load, $-mg$, where m is the mass of the load and g is the acceleration due to gravity.

$$\sum F_z = +\text{Force} - \text{Weight} = +F - mg = 0$$

The sign on the weight is negative for a coordinate system opposite the direction of gravitational acceleration. The z-subscript indicates that we are only examining the z-direction forces. As long as the load is stationary, there is no change in the energy. If, however, the load is raised from position (1) to (2) then the mechanical energy of the load is changed due to the work applied to the *system*, which in this case is the suspended mass. The work applied is:

$$\text{Work} = \int_1^2 F dz$$

Raising the load from z_1 to z_2 requires a constant force that is equal to the weight. With m and g being constant with respect to distance, work is:

$$\text{Work} = -mg \int_1^2 dz = -mg(z_2 - z_1) \quad (13.1)$$

Notice the sign on the work. It is negative because g is in the negative z-direction and Δz is positive when the weight is raised. If the load would have been lowered, then $z_2 - z_1 < 0$ and the work would have been positive. Therefore, work applied is negative in magnitude.

Equation 13.1 is a reduced form of the First Law of Thermodynamics. The left side is the *transitional energy* (work). The right side, $mg\Delta z$, is the change in *stored energy*.

Article 13 Engineering Thermodynamics

By extension, a more complete form of the First Law of Thermodynamics includes two transitional forms and two stored (accumulation) forms of energy; one thermal and one mechanical.

$$\underbrace{{}_1Q_2 - {}_1W_2}_{\text{transitional}} = \underbrace{\Delta U + mg\Delta z}_{\text{stored energy}}$$

13.3.2 Kinetic Energy

A word of caution about the previous discussion on gravitational potential energy; the relationships are only true if the load is raised so slowly that the velocity is constant over the entire time and there is no velocity at the position (1) and (2). In other words, only the static change in gravitational potential energy is considered. If at position (2) the load is still moving upwards at some velocity V_2 , then the stored mechanical energy must include a second energy term which is inertia. This is Newton's Second Law,

$$\sum F_z = F - mg = ma, \quad (13.2)$$

where a is the acceleration required to bring the system (suspended mass) from a stationary position (1) to a constant velocity at position (2). The right side equation 13.2, product of mass and acceleration, is the inertia of the load. In order to get the load moving the force must be greater than the weight due to the inertia of the load. For this scenario, work is balanced by two forms of energy storage:

$$\text{work} = \int_1^2 F dz = \int_1^2 mg dz + \int_1^2 ma dz$$

The gravitational potential integral is the same as in equation ???. The integral of inertia will result in a second mechanical energy term, but first we will need to examine the relationship between acceleration and displacement.

Acceleration is the time rate of change of velocity, $a = dV/dt$ and velocity is the time rate of change of position, $V = dz/dt$. We would like to integrate force with respect to distance (dz) instead of time. Velocity can be related to the change in position through the use of the chain-rule.⁴

$$a = \frac{dV}{dt} = \frac{dV}{dz} \frac{dz}{dt} = \frac{dV}{dz} V$$

Substituting this expression for acceleration into the inertia integral and recognizing that mass m is constant with respect to distance z .⁵

$$\int_1^2 m \left(V \frac{dV}{dz} \right) dz = m \int_1^2 V dV = \frac{1}{2} m (V_2^2 - V_1^2)$$

⁴The derivation of this expression for acceleration is rooted in particle dynamics, which is covered in detail in elementary physics courses as well as MEEM 2700 - Dynamics. The partial derivatives in this scenario are equivalent to total derivatives because the motion is limited to a single coordinate direction and the velocity is held constant after the initial acceleration.

⁵The theory of relativity ($\Delta E = \Delta mc^2/g_c$) shows that raising a mass increases the mass, but the increase is not measurable. Raising a 1 kg mass by 1 meter under terrestrial gravitation results in an mass increase of $1.09 \cdot 10^{-16}$ kg.

13.3 Accumulation of Mechanical Energy

Thus, the work required to raise the load from a resting position (1) to position (2) with a constant velocity is:

$${}_1W_2 = \underbrace{mg(z_2 - z_1)}_{\substack{\text{change in gravitational} \\ \text{potential energy}}} + \underbrace{\frac{1}{2}mV_2^2}_{\substack{\text{change in kinetic} \\ \text{energy}}}$$

Incorporating kinetic energy into the First Law of Thermodynamics results in three energy accumulation terms, one thermal and two mechanical.

$${}_1Q_2 - {}_1W_2 = \underbrace{\Delta U + mg\Delta z + \frac{1}{2}m(V_2^2 - V_1^2)}_{\text{stored energy}}$$

13.3.3 Elastic-Strain Energy

Another form of stored mechanical energy is that associated with compression or extension of a spring. Work applied to the spring becomes stored energy within the spring. This type of stored mechanical energy is *elastic-strain energy*. If the spring is allowed to expand, then work is recovered (force times distance) from the stored energy.

The force required to compress a simple spring is linearly proportional to the distance compressed,

$$F = k\Delta x,$$

where k is the constant of proportionality known as the spring constant with dimensions of force per length and typical units of lbf/ft or N/m. As long as the deformation is elastic (as opposed to plastic), then elastic-strain energy stored in the spring is recoverable. That is, if the spring is allowed to expand to the original position then the work recovered is the same as the original work expended.

The work of compression is

$$\text{Work} = \int_1^2 k(x_0 - x) dx,$$

where x_0 is the uncompressed spring length and x is the compressed length. For convenience, the displacement $(x_0 - x)$ will be rewritten as strain $\epsilon \equiv (x_0 - x)/x_0$, which is dimensionless (all units cancel out).

$$\text{Work} = \int_1^2 kx_0 \left(\frac{x_0 - x}{x_0} \right) dx = \int_1^2 kx_0 \epsilon dx$$

Using the chain rule from calculus, $dx \equiv -x_0 d\epsilon$, and the work required to compress a spring is more simply expressed as:

$$\text{Work} = -kx_0^2 \int_1^2 \epsilon d\epsilon = -\frac{1}{2}kx_0^2 (\epsilon_2^2 - \epsilon_1^2) \quad (13.3)$$

Article 13 Engineering Thermodynamics

The spring constant k is related to the modulus of elasticity and cross sectional area of the wire for compression springs. For torsional springs k is related to the shear modulus of elasticity.

Unlike gravitational potential and kinetic energy, the system boundary must be deformed in order to affect a change in this mechanical energy. Adding this form of mechanical energy to the First Law of Thermodynamics:

$${}_1Q_2 - {}_1W_2 = \underbrace{\Delta U + mg\Delta z + \frac{1}{2}m(V_2^2 - V_1^2)}_{\text{stored energy}} + \overbrace{\frac{1}{2}kx_0^2(\epsilon_2^2 - \epsilon_1^2)}^{\text{deformation}}$$

13.3.4 Flow Potential

The First Law of Thermodynamics is a subset of Conservation of Energy with a focus on thermal and mechanical energies. Like all conservation laws, it is only applicable to a fixed mass in a non-inertial frame of reference.⁶ Work and/or heat is applied across the boundary separating system from surroundings. The result may be a change in stored energy in the system.

In a heat engine, we are interested in the expansion of a compressed gas or steam through a work-producing device such as a piston-cylinder expansion or expansion through a turbine. The change in energy of the gas or steam during expansion can partially be explained by internal energy, but not completely. There is also a change in another form of mechanical energy, which we will call *flow potential*.⁷

In Figure 13.3, a fixed mass of steam is tracked as it passes through a turbine. At time t_1 , this mass is highly compressed with a large potential (relative to the surroundings) for flow. Then the steam expands, produces work, and arrives at a new energy state at time t_2 . The exchange of stored energy for work output is similar to that of a spring. The boundary of the system must be deformed to realize a work output.

Consider the compression of a metal bar of length L with an equal force applied at both ends. The strain in the bar due to the force will be $\epsilon = \Delta x/L$, where Δx is the change in length of the compressed bar. The work required to compress the bar is equal to the force times the displacement.⁸

$$\text{Work} = F\Delta x = FL\epsilon$$

The force applied to the ends of the bar can be expressed as a normal stress using the

⁶Non-inertial frame of reference implies a constant relative velocity of the *system* relative to the *observer*. Most often, this relative velocity is zero.

⁷Flow potential is used here to indicate that the change is only dependent upon the end states of the process and not the process itself. *Flow Work* is commonly used as well to distinguish between boundary work, but this can be confusing since a change in flow potential is only manifested through deformation of a system boundary.

⁸This simplified analysis assumes that the loading is uniaxial, the material is homogeneous with isotropic properties, there is no transverse deflection (bending) or buckling, the cross sectional area is uniform, and the compression is elastic.

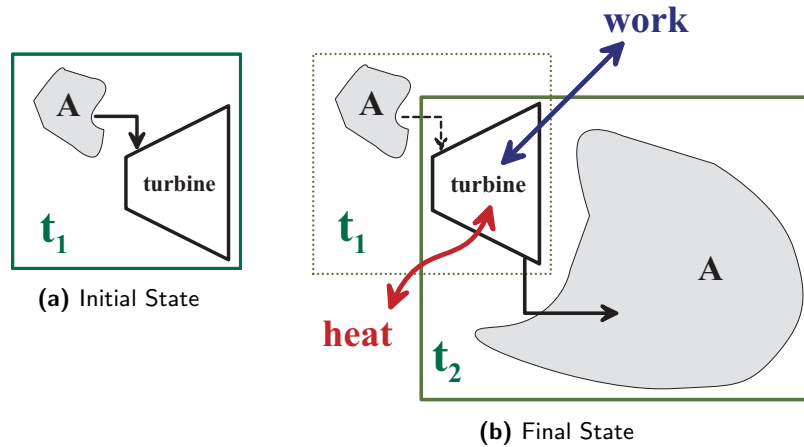


Figure 13.3. Expansion of steam through a turbine; system boundary is deformed.

cross-sectional area, $\sigma = F/A$.

$$\text{Work} = \sigma LA\epsilon$$

By examination, the length multiplied by the cross sectional area is volume, \forall , and volume multiplied by the strain is the change in volume, $\Delta\forall$. Thus, work of compression that is converted into strain-energy is simply the normal stress multiplied by the volume change:

$${}_1W_2 = \sigma(\forall_2 - \forall_1)$$

Pressure is a normal stress in fluids with the same units as stress, force/area. Compressing the steam stores the work of compression as a change in mechanical energy,

$$-{}_1W_2 = P_2\forall_2 - P_1\forall_1.$$

This form of stored mechanical energy is known as *flow potential*. Steam and air have an internal pressure for most engineering applications.⁹ So there is always some flow potential ($P\forall$) available.

Flow potential can easily be confused with boundary work as measured by an engine indicator. Both represent a deformation in the boundary separating the system and surroundings. The difference is that boundary work is path dependent. There may be more or less efficient paths. A change in flow potential, however, is only the difference between the two end states of the steam (or gas) independent of the work path affecting the change.

⁹The exceptions to the concept of internal pressure are limited to extremely low vacuum pressures or extremely small volumes. For both scenarios, the mean free path of any gas molecule becomes comparable to the size of the volume. Mean free path is the distance traveled by a gas molecule before reflecting off of another gas molecule or a surface.

Article 13 Engineering Thermodynamics

Including this fourth form of stored mechanical energy to include in the First Law of Thermodynamics:

$${}_1Q_2 - {}_1W_2 = \underbrace{\Delta U + mg\Delta z + \frac{1}{2}m(V_2^2 - V_1^2)}_{\text{stored energy}} + \overbrace{\frac{1}{2}kx_0^2(\epsilon_2^2 - \epsilon_1^2) + (P_2V_2 - P_1V_1)}^{\text{boundary deformation}} \quad (13.4)$$

13.3.5 Magnetic Potential

- [leave for later development](#)
- [cryogenic refrigeration](#)

13.4 First Law of Thermodynamics

In summary, the First Law of Thermodynamics is a balance between transitional energy (crossing a system boundary) and the change in stored energy in the system.

$${}_1Q_2 - {}_1W_2 = E_2 - E_1, \quad (13.5)$$

where E is the energy stored in *system* at equilibrium. Equilibrium implies that the energy throughout the system (fixed mass of interest) is not changing.

$$E = U + mgz + \frac{1}{2}mV^2 + \overbrace{\frac{1}{2}kx_0^2\epsilon^2 + P\forall}^{\text{deformation}} \quad (13.6)$$

When there is no deformation of the system boundary, then the last two energy terms do not undergo any change. The stored energies contained in E , shown in equation 13.6, are not all encompassing. We can add chemical energy, electrical energy, and nuclear energy if those forms were to experience significant change for the process being modeled.

Often it is convenient to work with specific energies, that is, energy per unit mass. There are several ways to quantify mass during energy conversion processes. If we are considering a fixed mass (system), then mass m can often be used directly. The total mass in a closed system is proportional to the volume of the system, $m \sim \forall$. The constant of proportionality is density ρ , which has units of mass per volume [kg/m³]. The inverse of density is specific volume v with units of [m³/kg]. Other commonly used measures of mass are specific gravity, $SG = \rho/\rho_{water}$, which is the fluid density normalized by the density of water at room temperature and specific weight, $\gamma = \rho g$, where g is acceleration due to gravity.

Lower case symbols will be used to indicate specific properties (properties per mass) such as $u = U/m$. The specific form of flow potential can be expressed as

$$\frac{P\forall}{m} = Pv \quad - \text{ or } - \quad \frac{P\forall}{m} = \frac{P}{\rho}$$

The specific form of stored energy (equation 13.6) can be written as:

$$e = \frac{E}{m} = \left(u + \frac{P}{\rho} \right) + \frac{V^2}{2} + gz + \frac{1}{2} \frac{kx_0 c^2}{\rho A} \quad (13.7)$$

When using the First Law of Thermodynamics to investigate heat engines, the forms of stored energy that are of most often of interest are the internal energy u (thermal) and the flow potential P/ρ (mechanical). Any time there is flow, such as steam through a boiler, condenser or turbine, then both of these stored energies will change.

13.5 Enthalpy

Engineers found in many processes that calculation of the change in stored energy required both internal energy and flow potential. So much so that for convenience the sum of these two energies was tabulated as a function of temperature and pressure for water and steam. Because internal energy is a thermodynamic property as are pressure and density, this summation $u + P/\rho$ is also a thermodynamic property.

This new property was called by many names including total heat, heat content, and heat of liquid. In the July 1936 issue of *Mechanical Engineering*, published by the American Society of Mechanical Engineers (ASME), the term *enthalpy* was selected to designate the thermodynamic function defined as internal energy plus the pressure volume product (or pressure divided by density) of any working substance. Enthalpy is from the Greek word "enthalpo", which means "heat within". The original symbol used to designate enthalpy was I, i . The use of I is still common nomenclature in the heating, ventilation and air conditioning (HVAC) industry. In mechanical engineering, H is the typical symbol for *enthalpy*.

$$H = U + P\forall \quad [\text{kJ, Btu}]$$

and on a per mass basis

$$h = u + Pv = u + \frac{P}{\rho} \quad \left[\frac{\text{kJ}}{\text{kg}}, \frac{\text{Btu}}{\text{lbm}} \right]$$

13.6 Rate of Energy Change

Consider the process where steam is moving through a condenser continuously – water vapor in and liquid water out. Application of conservation of energy (First Law of Thermodynamics) is for a fixed mass of steam. What is the mass of steam at time t_1 ? And can we locate that exact same mass later at time t_2 ? In this scenario, defining a “system” is difficult if not impossible. If the flow of steam through the condenser is steady, then it is much more convenient to compute the rate energy change.

Consider the scenario shown in Figure 13.3. The change in stored energy of the steam can be viewed from a rate perspective by examining the intersection of the system (A) at time t_1 and t_2 . This is illustrated in Figure 13.4.

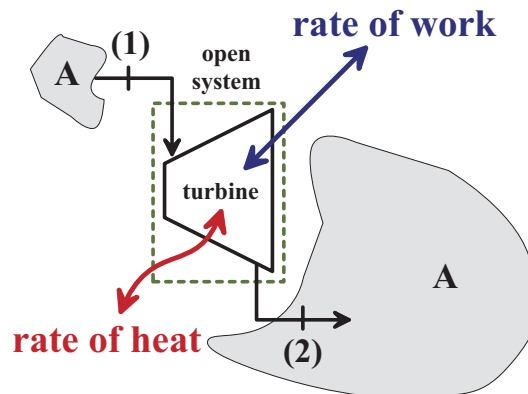


Figure 13.4. Examining Figure 13.3 from a rate perspective.

For this system, with steady flow through the turbine the First Law of Thermodynamics can be transformed into a rate equation:¹⁰

$$\dot{Q} - \dot{W} = \dot{m}_2 e_2 - \dot{m}_1 e_1 \quad (13.8)$$

where the dotted variable indicates a time derivative. For steady flow, conservation of mass dictates that $\dot{m}_1 = \dot{m}_2 = \dot{m}$, so the rate equation can be further simplified to

$$\dot{Q} - \dot{W} = \dot{m} (e_2 - e_1), \quad (13.9)$$

or in specific form (everything per mass),

$$q - w = e_2 - e_1, \quad (13.10)$$

where $q = \dot{Q}/\dot{m}$.

¹⁰Steady flow is an important restriction. Strictly speaking, conservation of energy is not applicable to the volume of space occupied by the turbine. Rather, it is applicable to the mass that flows through the turbine over a fixed period of time as shown in Figure 13.3. If the flow is not steady, then mass and energy may be accumulating inside this volume and the expression of the First Law on an open system (rate equation) is not valid. Control volume analysis can be utilized for unsteady flow.

We can expand the First Law of Thermodynamics to include multiple mass flow inlets and exits as shown in Figure 13.5. Each inlet and exit has a corresponding energy and mass that must be taken into account. This means that two relationships are necessary; conservation of energy (First Law of Thermodynamics) and conservation of mass.

$$\sum \dot{Q} - \sum \dot{W} = \sum_{\text{out}} \dot{m}e - \sum_{\text{in}} \dot{m}e \quad (13.11)$$

$$0 = \sum \dot{m}_{\text{out}} - \sum \dot{m}_{\text{in}} \quad \text{— or, for Fig. 13.5 —} \quad \dot{m}_3 = \dot{m}_1 + \dot{m}_2 \quad (13.12)$$

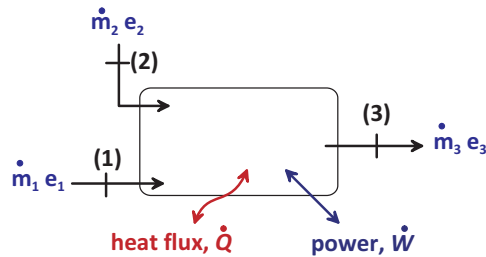


Figure 13.5. Control volume with multiple inlets and exits.

When considering heat engines, the energy change of interest is often limited to changes in internal energy and flow potential, which is combined into enthalpies. Therefore, ΔE reduces to ΔH and changes in kinetic, gravitational potential, and elastic-strain can be safely neglected.

13.6.1 Useful Simplification to Rate Equation

Consider the rate forms of conservation of mass and energy on a steady process with a single inlet and exit.

$$\dot{Q} - \dot{W} = \dot{m}_{\text{exit}} e_{\text{exit}} - \dot{m}_{\text{inlet}} e_{\text{inlet}} \quad \text{— and —} \quad \dot{m}_{\text{exit}} = \dot{m}_{\text{inlet}} = \dot{m}$$

These two expressions can be combined to form a single energy balance in terms of specific energies by dividing both sides of the energy equation by the mass flow rate.

$$q - w = e_{\text{exit}} - e_{\text{inlet}}$$

The change in stored energy Δe may include any combination of thermal or mechanical energies as shown in equation 13.7.

Now consider the rate forms of conservation of mass and energy applied to a process illustrated in Figure 13.5. The mass flow rate is not the same at each inlet and outlet. Nevertheless, we can still simplify conservation of energy by incorporating conservation of mass. Conservation of mass can be rewritten in terms of ratios:

$$\dot{m}_3 = \dot{m}_1 + \dot{m}_2 \quad \implies \quad 1 = \frac{\dot{m}_1}{\dot{m}_3} + \frac{\dot{m}_2}{\dot{m}_3}$$

Dividing conservation of energy by the total mass flow rate, which in this case is \dot{m}_3 ,

$$q - w = e_3 - \left(\frac{\dot{m}_1}{\dot{m}_3}\right) e_1 - \left(\frac{\dot{m}_2}{\dot{m}_3}\right) e_2$$

This approach is useful when calculating energy changes of two fluid streams that are mixing. For example, if there is no heat or work ($q = w = 0$) in the scenario shown in Figure 13.5 and the inlet energies and mass flow rates are known, the specific energy at the exit is

$$e_3 = \left(\frac{\dot{m}_1}{\dot{m}_3}\right) e_1 + \left(\frac{\dot{m}_2}{\dot{m}_3}\right) e_2$$

If 20% of the total mass flow exiting at (3) is from (1), the energy entering at (1) is scaled by 0.20.

13.7 Measurable Properties and Changes in Energy

As a general rule, we can only measure changes in energy. There is no method by which we can measure the absolute energy; we can only measure energy relative to another state or reference, and then only through inference. An example is the closed system heat addition to an ideal gas discussed in §13.7.1. The total energy transferred to the tank containing the ideal gas can be calculated by knowing the heat transfer rate, or power, and the duration of applying that power.

$$Q_{\text{in}} = \dot{Q}_{\text{in}} \Delta t$$

An example would be heat addition via an electric heater in which the electrical power is measured. From the First Law of Thermodynamics (Conservation of Energy), the heat input is equal to the change in the energy of the ideal gas:

$$Q_{\text{in}} = U_2 - U_1 = m_{\text{gas}} (u_2 - u_1)$$

As heat is added, the measured temperature of the gas increases in proportion to the quantity of heat.

$$Q_{\text{in}} \sim T_2 - T_1 = c (T_2 - T_1),$$

where c is a constant of proportionality. This particular constant of proportionality between heat addition and temperature increase is known as specific heat. Thus, by carefully designing and controlling the process of energy change, which in this case is a constant volume (isochoric) process, the change in energy as expressed using the first law of thermodynamics can be related to a change in the measurable property temperature.

13.7.1 Specific Heats (c , c_v , c_p)

In order to relate changes in thermal energy to something measurable, a process must be defined using conservation of energy and mass that only results in changes of interest. Beginning with simple compressible substances such as air or an ideal gas, an experiment can be designed such that conservation of energy reduces to:

$$\underbrace{Q}_{\text{transitional}} = \underbrace{m\Delta u}_{\text{stored in gas}}, \quad (13.13)$$

Such an experiment is shown in Figure 13.6. Heat is applied to a constant volume container holding a gas. By design, there is no change in kinetic energy or gravitational potential. Because the boundary of the system (gas) does not deform there is also no change in elastic-strain or flow potential. The only stored energy that changes is thermal. For this experiment, no work is applied. Temperature of the gas is measured during heat transfer to the gas. The resulting data shows a linear relationship between the amount of heat added and the change in temperature.¹¹ Conservation of energy for

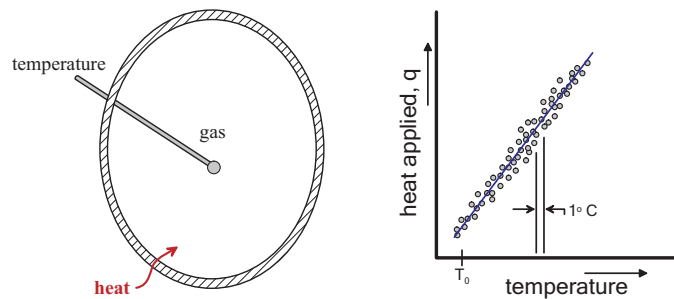


Figure 13.6. Conceptual experiment (calorimetry) for determining relationship between stored thermal energy and temperature.

this experiment is

$$q_{\text{in}} = \frac{Q_{\text{in}}}{m_{\text{gas}}} = \delta u = c \Delta T,$$

where c is a proportionality constant. That is, c is the slope of the experimental data. For infinitesimal changes,

$$\delta q_{\text{in}} = du = c dT$$

For this scenario, the proportionality constant c is known as the specific heat at constant volume and labeled c_v . The subscript v indicates the process (constant volume \equiv isochoric) used to measure this property.

A common misconception is that c_v can only be used when considering constant volume processes. Specific heats relate measurable property changes, in this case temperature, to changes in stored energy. Thus, c_v relates temperature changes to changes in internal energy regardless of the process being considered.

¹¹The result is linear only for small temperature changes unless the gas is ideal. Ideal gases include helium, argon, and neon.

13.7.2 Changes in Enthalpy

The identical approach can be used to relate changes in enthalpy to changes in temperature. The process to measure this relationship must be designed different in that the boundary must be allowed to deform. If we design a constant pressure process, such as a gas being heated in a piston-cylinder working against a constant force, then conservation of energy reduces to

$${}_1q_2 = h_2 - h_1 = (u_2 - u_1) + P(v_2 - v_1)$$

As heat is added to the gas, conservation of energy dictates that enthalpy increases and the measured temperature increases. The proportionality constant between Δh and ΔT is not the same as the between Δu and ΔT discussed above. In this scenario, the constant of proportionality is called the specific heat at constant pressure c_p .

$$\Delta h = c_p \Delta T \quad \text{— or, more precisely, —} \quad dh = c_p dT$$

As with c_v , there is often confusion with respect to when c_p can be used. It is not restricted to constant pressure processes. Rather, it is the proportionality constant between changes in enthalpy and temperature.

13.7.3 Specific Heats for an Ideal Gas

For an ideal gas, $Pv = RT$ (property relationship)

$$\tilde{h} = \tilde{u} + Pv = \tilde{u} + RT$$

$$c_v = \frac{d\tilde{u}}{dT}$$

$$c_p = \frac{d\tilde{h}}{dT} = \frac{d(\tilde{u} + RT)}{dT} = \frac{d\tilde{u}}{dT} + \frac{RdT}{dT} + \frac{TdR}{dT} \stackrel{R, \text{ constant}}{=} c_v + R$$

define $k \equiv \frac{c_p}{c_v}$ (also denoted as γ)

$$\left. \begin{aligned} c_p &= c_v + R \\ k &= \frac{c_p}{c_v} \end{aligned} \right\} \begin{aligned} c_p &= \frac{kR}{k-1} \\ c_v &= \frac{R}{k-1} \end{aligned}$$

13.7.4 Specific Heat for Liquids and Solids

For a gas, there is a distinct difference between a change in internal energy and a change in enthalpy because the flow potential (P/ρ) can be changed easily by expansion or compression. Liquids and solids are not so easy to compress. As a result, even though the volume of a liquid or solid may change slightly during heating or cooling, the change in flow potential is often negligible as compared to the change in internal energy. The net result is that for incompressible substances.

$$c_v = c_p$$

13.8 State Property Relationships

The primary properties that can be measured are pressure, temperature, volume and mass. Other useful properties can be derived from these four such as density ($\rho = \text{mass/volume}$) and specific volume ($v = \text{volume/mass}$). When there is no change in energy state of a system ($\Delta e = 0$), then measurable properties can be related to one another. Relationships between properties measured during a state of equilibrium are collectively known as *equations of state*.

On such state relationship is the Ideal Gas Law, where the product of pressure and volume is proportional to temperature for simple compressible gases.

$$Pv = RT,$$

where R is a constant of proportionality known as the gas constant. The ideal gas law is but one example of numerous relationships between properties of a substance in an equilibrium state, which again means that there is no change in energy occurring. Another example of such a property relationship is the Non-Ideal Gas Law.

$$Pv = ZmRT,$$

where Z is the *compressibility*, an experimentally determined factor that accounts for non-ideal compression of more complex gases such as butane.

An equation of state for an incompressible fluid (liquid) is $m \sim v = \rho v$. In this instance ρ is a constant of proportionality and it is not dependent upon temperature or pressure. In other words, this particular equation of state indicates that the fluid density is constant with respect to other thermodynamic properties.

There are many equations of state for gases, liquids and solids. When a substance is near the transition between vapor-liquid, liquid-solid, or solid-gas, then defining an equation of state becomes extremely difficult. In these cases, where the equilibrium state is near a phase transition, the relationship between properties is experimentally measured and tabulated.¹² Examples where tabulated property relationships are common include steam, refrigerants and gases that are near the boiling point such as hydrogen at 21 K. Steam tables include three sets of relationships, one for each phase:

- (i) vapor in equilibrium, known as superheated vapor, which does not behave as an ideal gas;
- (ii) vapor and liquid in equilibrium with one another, known saturated liquid/vapor, which can exhibit large changes in thermal energy without any change in temperature; and
- (iii) liquid in equilibrium, known as subcooled or compressed liquid, which does not necessarily behave as an incompressible liquid.

¹²Fluid phases can include solid, liquid, vapor, and critical.

Article 13 Engineering Thermodynamics

- latent heat
- least is known about subcooled liquid
- finish section with process of determining energy changes
- P-v diagram for steam

The relationship between measurable properties and energies are developed using a combination of:

1. fluid property relationships
2. first law of thermodynamics
3. heat transfer and fluid mechanics relationships (pitot-static measurement, hot-wire anemometry, ...)

13.8 State Property Relationships

- For a simple compressible substance (ideal gas, air, ...) and neglecting kinetic & potential energy changes,

$$Q - W = \Delta \tilde{U} = m \Delta \tilde{u}$$

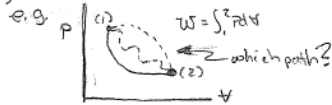
$$W \rightarrow \text{boundary work} \equiv F \Delta x = (P \cdot A) \Delta x = P \Delta V$$

$$Q \propto m \Delta T \leftarrow \text{Heat transfer is proportional to the mass and temperature difference.}$$

- On an infinitesimal basis,

$$\delta Q - \delta W = m d\tilde{u}$$

↑ not derivatives because these are path-dependent processes and we don't yet know the process:



$$\delta W = P dV$$

$\delta Q \propto m dT$ ← Use a constant of proportionality to turn this into an equality.

$$\delta Q = m c dT$$

1st Law:

$$\delta Q - \delta W = m c dT - P dV = m d\tilde{u} \quad (-m P dV)$$

Constant Volume Process

$$\delta W = P dV = 0; \text{ therefore } c_v = \left. \frac{d\tilde{u}}{dT} \right|_v$$

- c_v is the slope of $\tilde{u}(T)$
- Since c_v is only a function of properties (\tilde{u} & T), it too is a property!

Constant Pressure Process

$$\delta Q - \delta W = m d\tilde{u} \rightarrow \delta Q = m d\tilde{u} + m P dV$$

• recall enthalpy is defined as $\tilde{h} = \tilde{u} + P V$,

$$d\tilde{h} = d\tilde{u} + P dV + V dP \quad \& \quad dP = 0 \text{ for constant pressure process}$$

• Thus,

$$\delta Q = m c dT = m d\tilde{h}$$

$$\hookrightarrow c_p = \left. \frac{d\tilde{h}}{dT} \right|_p$$

- c_p is the slope of $\tilde{h}(T)$
- Since c_p is only a function of properties (\tilde{h} & T), it too is a property!

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