The first law of thermodynamics is the conservation of energy applied to thermal systems. The second law of thermodynamics states limitation on how much of a system’s thermal energy can be converted to other forms of energy.

Thermodynamic variables describe the state of the thermal system and the equation of state relates these variables. If we draw diagrams of $p - V$ or $p - T$ or $T - V$, the changes in the state of the system can be represented as curves (at least if thermal equilibrium is established at every stage of transformation).

**Reversible process** is one where thermal equilibrium is maintained throughout, such as the sufficiently slow compression of a piston in an insulated cylinder.

**Irreversible process** is one in which thermal system’s changes cannot be retraced, such as gas expanding to fill a vacuum through an open stopcock.

A thermodynamic system can transfer its internal energy by changing the temperature (or phase) of another system or it can use its internal energy to do mechanical work on its surroundings.

### 1. Heat Flow

1. Heat flow is a transfer of energy.
2. Thermal systems have internal energy related to the system’s thermal properties.

The connection between heat flow and temperature change is the *heat capacity*, $C$ (which is always positive). A small heat flow $dQ$ into a system will change the temperature by a small amount $dT$ with proportionality constant $C$:

$$dQ = CdT$$

The value of the heat capacity depends on the material and is proportional to the mass. We can define the specific heat $c$ as the heat capacity per unit mass ($dq = cdT$).

Note: If we decrease (increase) the heat flow from a substance with a large specific heat capacity, such as water, the temperature of the substance will fall
(rise) only slightly. This is why large bodies of water have strong moderating effects on the climate in their vicinity.

1a. Heat flow depends on the path

While heat capacity is defined in terms of temperature change, the conditions for temperature change are not unique. The proportionality constants between heat absorption and temperature change define the 1) specific heat capacity at constant pressure:

\[ c_p = \frac{dq_p}{dT} \]  \hspace{1cm} (2)

and the 2) heat capacity at constant volume:

\[ c_v = \frac{dq_v}{dT} \]  \hspace{1cm} (3)

where the subscript denotes isobaric and isochoric processes respectively.

Example: Transformation in \( P - V \) space following two different paths.

1b. Phase changes and heat flow

When there is phase change, there is no temperature change even though there is heat flow. The heat flow necessary to bring about the transformation from solid to liquid is the latent heat of fusion \( (L_f = 79.6\text{cal/g}) \) for ice. The heat flow goes into changing the molecular arrangement of the substance. The heat necessary to convert 1g of water at 100°C at 1 atm to 1 g of steam is called latent heat of vaporization \( (L_v = 540\text{cal/g}) \) which goes into breaking intermolecular forces.

1c. Mechanical equivalent of heat

Example: Joule’s churning paddle experiment.

As the paddles do a certain amount of work on the water, the temperature of the system will have risen by a definite amount. The experiment demonstrated that there is a precise equivalent between work done on a system and the heat flow into it, so heat flow is an energy transfer.

\[ 1\text{cal} = 4.185J \]  \hspace{1cm} (4)
2. Work done by Thermal Systems

If we restrict our analysis to a system comprised of a gas, and consider only work done by or on the gas by expansion or compression. The example of the cylinder of fixed cross-sectional area with a fitted movable frictionless piston (Fig 3.4). The pressure-volume thermodynamic diagram of the states of the system is also shown. As the piston moves outward an infinitesimal distance $dx$ the work done while its pressure remains essentially constant at $p$ is:

$$dW = Fdx$$
$$= pAdx$$
$$= pdV$$

2a. Work depends on the path

The work done by the substance when the volume increases by a small increment $dV$ is equal to the pressure of the substance multiplied by its increase in volume. In going from A to B, the work done by the material is equal to the area under the curve.

$$W = \int_{V_1}^{V_2} pdV$$

If $V_2 > V_1$, $W$ is positive and the substance does work on its environment. If $V_2 < V_1$, $W$ is negative and the environment does work on the substance.

Using specific properties:

$$dw = pd\alpha$$

If we think of the work done by a thermal system as the area under a curve of $p$ vs $V$, the fact that work done depends on the path of the change becomes evident.
3. Internal Energy

In thermal (internal) energy is associated with the energy of the molecules of a thermal system. Changes in internal energy, are not path dependent. This contrasts sharply with work or heat flow which are path dependent. So we can write:

$$\int_{A}^{B} dU = U_B - U_A$$  \hspace{1cm} (8)

We can’t actually do this with work or heat flow because we need to know the path. We will not change the mathematical notation of $dW$ or $dQ$, but keep in mind these are not true differentials. Internal energy is purely a function of state.

4. First Law of Thermodynamics

Let us imagine a closed system (in which the total amount of matter is kept constant), that receives a certain quantity of thermal energy $dQ$. Of the total amount of heat added to a gas, $dQ$, some may tend to increase the internal energy of the gas by an amount $dU$ and the remainder will cause work to be done by the gas in the amount $dW$. In algebraic form:

$$dQ = dU + dW$$  \hspace{1cm} (9)

It is more useful to express this equations in terms of specific properties (divide by mass) $z = Z/m$ where $Z$ is an extensive property that depends on the mass $m$ of the system, and $z$ is an intensive property that doesn’t depend on the mass.

$$dq = du + dw$$  \hspace{1cm} (10)

This is the mathematical formulation of the First Law of Thermodynamics and embodies three related ideas:

1. The existence of an internal energy function
2. The principle of conservation of energy
3. definition of heat as energy in transit

$$dq = du + pd\alpha$$  \hspace{1cm} (11)
note:
• Change of internal energy between two states is path independent, so the change of internal energy vanishes for cyclical processes.
• The work performed by the system and the heat transferred into it is path dependent

We can introduce the state variable enthalpy:

\[ h \equiv u + p\alpha \]  \hspace{1cm} (12)

\[ dh = du + d(p\alpha) = du + \alpha dp + p\alpha d\alpha \]  \hspace{1cm} (13)

and the first law in terms of enthalpy becomes:

\[ dh = dq + \alpha dp \]  \hspace{1cm} (14)

4a. Heat Capacity

The specific heat capacities are related closely to the internal energy and enthalpy of the system. Because they are state variables, \( u \) and \( h \) can be expressed in terms of any two other state variables. For instance \( u = u(\alpha, T) \)

\[ du = \left( \frac{\partial u}{\partial \alpha} \right)_T dv + \left( \frac{\partial u}{\partial T} \right)_\alpha dT \]  \hspace{1cm} (15)

Incorporating this into the first law:

\[ dq = \left( \frac{\partial u}{\partial T} \right)_\alpha dT + \left[ \left( \frac{\partial u}{\partial \alpha} \right)_T + p \right] d\alpha \]  \hspace{1cm} (16)

For an isochoric process this reduces to:

\[ \frac{dq_v}{dT} = \left( \frac{\partial u}{\partial T} \right)_\alpha = c_v \]  \hspace{1cm} (17)

This means that the heat capacity at constant volume measures the rate of internal energy change with temperature during and isochoric process.

In a similar fashion we can use enthalpy expressed as \( h = h(p, T) \):

\[ dq = \left( \frac{\partial h}{\partial T} \right)_p dT + \left[ \left( \frac{\partial h}{\partial T} \right)_T - \alpha \right] dp \]  \hspace{1cm} (18)
For an isobaric process this reduces to:

\[ \frac{dq_p}{dT} = \left( \frac{\partial h}{\partial T} \right)_p = c_p \]  

(19)

This means that the heat capacity at constant pressure measures the rate of enthalpy increase with temperature during and isobaric process. Over ranges of pressure and temperature relevant to the atmosphere, the specific heats may be regarded as constants for an ideal gas. The change of internal energy during an isochoric process is proportional to the change of temperature alone, and similarly for the change of enthalpy during an isobaric process.

4b. Joule’s Experiment (Internal Energy of Ideal Gases)

Two perfect gases at pressures \( p_1 \) and \( p_2 \) are brought into contact and allowed to equilibrate.

- No heat transfer takes place with the environment \( dq = 0 \).
- Volume of the system (of the two gases) doesn’t change \( dw = 0 \).
- Internal energy then doesn’t change \( du = 0 \).

There is no change in internal energy but the equilibrated pressure did change, so \( u \) isn’t a function of pressure. Consequently, \( u = u(T) \) and the internal energy is a function of temperature alone.

Integrating Equations 2 and 3 with respect to temperature yields finite values of internal energy and enthalpy, which are unique up to constants of integration. It is customary to define \( u \) and \( h \) so that they vanish at a temperature of absolute zero.

\[
\begin{align*}
    u &= c_v T \\
    h &= c_p T
\end{align*}
\]

(20, 21)

We can express the first law in terms of specific heat and using the ideal gas law \( d(p\alpha) = RdT \)

\[ c_p - c_v = \frac{h - u}{T} = \frac{p\alpha}{T} = R \]  

(22)
For a monoatomic gas $c_v = \frac{3}{2}R$, for a diatomic gas $c_v = \frac{5}{2}R$, since air is mainly diatomic.

Specific heats for dry air:

- $c_v = 1004.5\,\text{JK}^{-1}\,\text{kg}^{-1}$
- $c_v = 717.5\,\text{JK}^{-1}\,\text{kg}^{-1}$

And we define the dimensionless constants

$$\gamma = c_p/c_v = 1.4 \quad (23)$$

$$\kappa = R/c_p \approx 0.286 \quad (24)$$

To summarize, the first law can be expressed as

$$dq = c_vdT + pd\alpha \quad (25)$$

$$dq = c_pdT - \alpha dp \quad (26)$$

For isochoric and isobaric processes reduce to:

$$dq_v = c_vdT \quad (27)$$

$$dq_p = c_pdT \quad (28)$$

4c. Adiabatic Processes

If a material undergoes a change in its physical state without any heat being added or withdrawn from it, the change is said to be adiabatic. For an adiabatic process, the first law reduces to

$$0 = c_vdT + pd\alpha \quad (29)$$

$$0 = c_pdT - \alpha dp \quad (30)$$

Dividing through by T and introducing the gas law transforms
\[
0 = c_v d \ln T + Rd \ln \alpha \\
0 = c_p d \ln T - Rd \ln p \\
0 = c_v d \ln p + c_p d \ln \alpha
\] (31)

which can be integrated to obtain Poisson’s equations that define adiabatic paths in the state space of an ideal gas. This means that the change in a single state variable, together with the condition that the process be adiabatic determines the change of a second state variable. Adiabatic system possesses only one independent state variable and only one thermodynamic degree of freedom.

\[
T \alpha^{\gamma-1} = \text{const} \\
T \rho^{-\kappa} = \text{const} \\
p \alpha^{\gamma} = \text{const}
\] (34) (35) (36)

Poisson’s equations describe a family of contours known as adiabats in the plane of any two of the state variables \( p, T \) and \( \alpha \) in the same way that isobars describe isobaric processes, isotherms describe isothermal processes and isochores describe isochoric processes.

4d. Potential Temperature

Potential temperature \( \theta \) is defined as the temperature assumed by the system when compressed or expanded adiabatically to a reference pressure of \( p_0 = 1000 \text{mb} \). Using Poisson’s equation 36, an adiabatic process from state \( (p, T) \) to the reference state \( (p_0, \theta) \) is

\[
\theta p_0^{-\kappa} = T \rho^{-\kappa}
\] (37)

So the potential temperature is described by

\[
\theta = T \left( \frac{p_0}{p} \right)^\kappa
\] (38)

Theta is a state variable and invariant along an adiabatic path in state space. Adiabatic behavior is a good approximation for many atmospheric applications because over a fairly large scale of motions, the timescale for an air parcel to adjust to changes of pressure and to perform expansion work is short compared to
Figure 1: Salby 2.8
the characteristic timescale of heat transfer.

4e. Meteorological Thermodynamic Charts

i. Adiabatic chart (Stuve Diagram) Based on the adiabatic equation 38, is based on the linear relation between $T$ and $p^\kappa$. Adiabatic processes follow straight line paths on a thermodynamic diagram with coordinates of $T$ vs $p^\kappa$.

![Stuve diagram](image)

**Figure 2:** Rogers and Yau, 1.4

ii. Skew T-log p Diagram One way to display these changes is on a Skew T-ln p chart. On this chart, dry adiabats are slightly curved lines that run from the lower right to the upper left with an angle between isotherms and dry adiabats of approx $90^\circ$. This diagram was developed by the US Air Force in 1952.

4f. Dry Adiabatic Lapse Rate

Remember, for an adiabatic process

\[
\frac{c_p dT}{dp} = \frac{\alpha}{c_p} = \frac{1}{\rho c_p} \quad \text{(39)}
\]

\[
\frac{dT}{dp} = \frac{\alpha}{c_p} = \frac{1}{\rho c_p} \quad \text{(40)}
\]
Since
\[ \frac{dT}{dz} = \frac{dT}{dp} \frac{dp}{dz} = -\frac{1}{\rho c_p} \rho g = -\frac{g}{c_p} = -\Gamma \] (41)

\( \Gamma = 9.8^\circ C km^{-1} \) is the dry adiabatic lapse rate. This shows that as the air parcel ascends (descends) dry adiabatically, its temperature decreases (increases) at the fixed rate of nearly 10\(^\circ\)C per km.

4g. Diabatic Processes

Under diabatic conditions, the system interacts with its environment thermally as well as mechanically. This occurs near the surface (thermal conduction and turbulent mixing) or inside clouds due to the release of latent heat. The potential temperature of an air parcel is then no longer conserved, but now \( \theta \) changes in proportion to heat transferred into the system. The increase of potential temperature is a direct measure of the heat transferred into the system.