First Law of Thermodynamics

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The first law of thermodynamics is the conservation of energy applied to thermal systems.

Here, we develop the principles of thermodynamics for a discrete system, namely, an air parcel moving through the circulation. A thermodynamic system can transfer its internal energy by changing the temperature (or phase) of another system of it can use its internal energy to do mechanical work on its surroundings.

Two types of properties characterize the state of a system. Some of them depend on mass:

Intensive properties Do not depend on mass - like pressure and temperature

Extensive properties Depend on mass - like volume

Transformation An intensive property z can be defined from an extensive property Z by dividing by mass of the system m so $z = Z/m$, and the intensive property is referred to as a specific property.

Thermodynamic variables describe the state of the thermal system, and the ideal gas law relates these variables. We can very usefully describe the state as a point on a two-dimensional plot, such as a p-V diagram, a p-T diagram, or a V-T diagram. Changes, or transformations in the state of a thermal system can be represented as curves on such diagrams - at least if thermal equilibrium is established at every stage of the transformation. A change in which thermal equilibrium is maintained throughout, such as the sufficiently slow compression of a piston in an insulated cycling is called a **reversible process**. Conversely, a gas expanding

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

Irreversible processes Is one in which the system's changes cannot be retraced, such as gas expanding to fill a vacuum through an open stopcock.

1. Heat Flow

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

Heat transfer can happen via diffusion, thermal conduction or radiation, for an open system it can occur through absorption of water vapor (latent heat). For many applications, heat transfer is secondary to processes introduced through motion, which operate on timescales of order one day and shorter (particularly in the boundary layer) In the free atmosphere and away from clouds, the prevailing form of heat transfer is radiative. Operating on a timescale of order weeks. If no heat is exchanged between a system and its environment, the process is adiabatic, and diabatic otherwise. Adiabatic approximation is a good approx. in many cases because heat transfer is slow compared to motion.

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:

$$dQ = CdT \tag{1}$$

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*:

$$c_p = \frac{dq_p}{dT} \tag{2}$$

and the *2) heat capacity at constant volume*:

$$c_v = \frac{dq_v}{dT} \tag{3}$$

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* ($L_f = 79.6 cal/g$ 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* ($L_v = 540 cal/g$) 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.

$$1 cal = 4.185 J \tag{4}$$

Mechanical Equivalent of heat

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:

$$\begin{aligned} dW &= Fdx \qquad (5) \\ &= pAdx \\ &= pdV \end{aligned}$$

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.

$$W = \int_{V_1}^{V_2} pdV \qquad (6)$$

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:

$$dw = pd\alpha \qquad (7)$$

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:

$$\int_{A}^{B} dU = U_B - U_A \tag{8}$$

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:

$$dQ = dU + dW \tag{9}$$

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.

$$dq = du + dw \tag{10}$$

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

$$dq = du + pd\alpha \tag{11}$$

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*:

$$h \equiv u + p\alpha \tag{12}$$

$$dh = du + d(p\alpha) = du + \alpha dp + p d\alpha \tag{13}$$

and the first law in terms of enthalpy becomes:

$$dh = dq + \alpha dp \tag{14}$$

4a. *Joule's Experiment (Internal Energy of Ideal Gases)*

Two *perfect* gases at pressures $p1$ and $p2$ 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 infernal energy is a function of temperature alone and enthalpy is a function of temperature alone $h = h(T)$.

4b. *Heat Capacity*

The specific heat capacities are related closely to the internal energy and enthalpy of the system.

$$dq = du + p d\alpha \tag{15}$$

For an isochoric process this reduces to:

$$\frac{dq_v}{dT} = \left(\frac{\partial u}{\partial T}\right)_\alpha = c_v \tag{16}$$

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 $h = h(T)$:

$$dq = dh - \alpha dp \tag{17}$$

For an isobaric process this reduces to:

$$\frac{dq_p}{dT} = \left(\frac{\partial h}{\partial T}\right)_p = c_p \tag{18}$$

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.

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.

$$u = c_v T \tag{19}$$

$$h = c_p T \tag{20}$$

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

$$c_p - c_v = \frac{h - u}{T} = \frac{p\alpha}{T} = R \tag{21}$$

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:

- $c_v = 1004.5 J K^{-1} kg^{-1}$
- $c_v = 717.5 J K^{-1} kg^{-1}$

And we define the dimensionless constants

$$\gamma = c_p/c_v = 1.4 \tag{22}$$

$$\kappa = R/c_p \approx 0.286 \tag{23}$$

To summarize, the first law can be expressed as

$$\begin{aligned} dq &= c_v dT + p d\alpha && (24) \\ dq &= c_p dT - \alpha dp && (25) \end{aligned}$$

For isochoric and isobaric processes reduce to:

$$\begin{aligned} dq_v &= c_v dT && (26) \\ dq_p &= c_p dT && (27) \end{aligned}$$

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

$$\begin{aligned} 0 &= c_v dT + p d\alpha && (28) \\ 0 &= c_p dT - \alpha dp && (29) \end{aligned}$$

Dividing through by T and introducing the gas law transforms

$$\begin{aligned} 0 &= c_v d \ln T + R d \ln \alpha && (30) \\ 0 &= c_p d \ln T - R d \ln p && (31) \\ 0 &= c_v d \ln p + c_p d \ln \alpha && (32) \end{aligned}$$

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, ogether with the condition hat 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.

$$
\begin{aligned}
T\alpha^{\gamma-1} &= const \qquad (33)\\
Tp^{-\kappa} &= const \qquad (34)\\
p\alpha^{\gamma} &= const \qquad (35)
\end{aligned}
$$

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

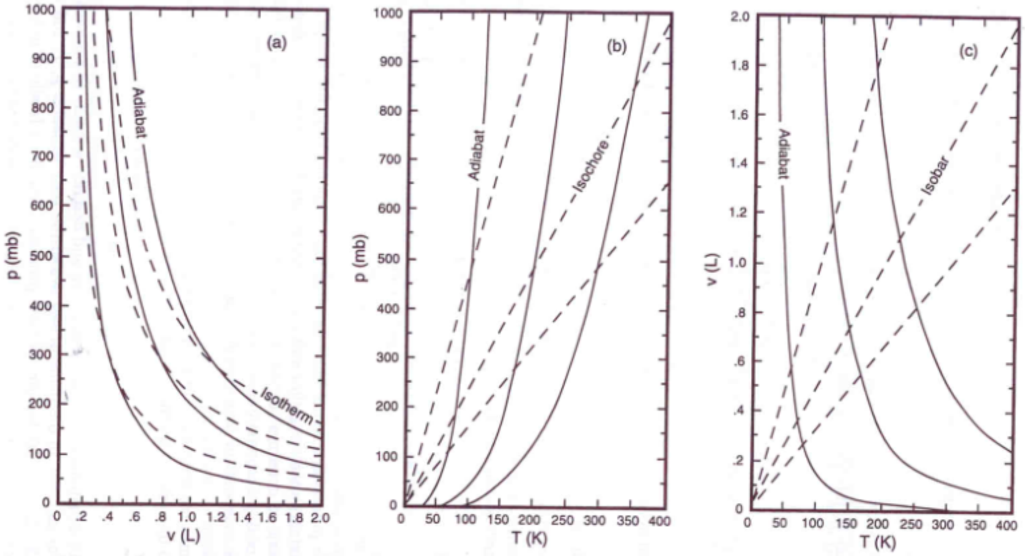

Figure 2.8 Changes of pressure, volume, or temperature in terms of one other state variable during an adiabatic process, which define *adiabats* in the state space of an ideal gas. Also shown are the corresponding changes during an isothermal process (T = const), an isochoric process (v = const), and an isobaric process (p = const), which define *isotherms*, *isochores*, and *isobars*, respectively.

Figure 1: Salby 2.8

4d. *Potential Temperature*

Potential temperature θ is defined as the temperature assumed by the system when compressed or expanded adiabatically to a reference pressure of $p_0 = 1000mb$. Using Poisson's equation 35, an adiabatic process from state (p, T) to the reference state (p_0, θ) is

$$\theta p_0^{-\kappa} = Tp^{-\kappa} \tag{36}$$

So the potential temperature is described by

$$\theta = T\left(\frac{p_0}{p}\right)^{\kappa} \tag{37}$$

Theta is a state varaible 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 ant to perform expansion work is short compared to the characteristic timescale of heat transfer.

4e. *Meteorological Thermodynamic Charts*

i. Adiabatic chart (Stuve Diagram) Based on the adiabatic equation 37, is based on the linear relation between T and p^{κ}. Adiabatic processes follow straight line paths on a thermodynamic diagramwit hcoordinates of T vs p^{κ}

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°. This diagram was developed by the US Air Force in 1952

4f. *Dry Adiabatic Lapse Rate*

Remember, for an adiabatic process

$$\begin{aligned} c_p dT &= \alpha dp & (38) \\ \frac{dT}{dp} &= \frac{\alpha}{c_p} = \frac{1}{\rho c_p} & (39) \end{aligned}$$

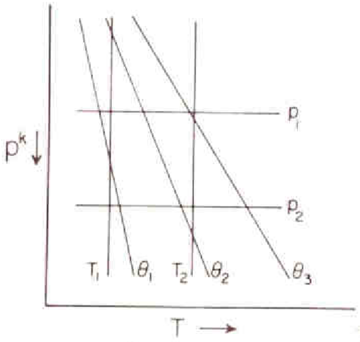

FIG. 1.4. Stüve diagram.

Figure 2: Rogers and Yau, 1.4

Since

$$\frac{dT}{dz} = \frac{dT}{dp}\frac{dp}{dz} = -\frac{1}{\rho c_p}\rho g = -\frac{g}{c_p} = -\Gamma \tag{40}$$

$\Gamma = 9.8°Ckm^{-1}$ 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 $10°C$ 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 turbulen 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 θ 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.

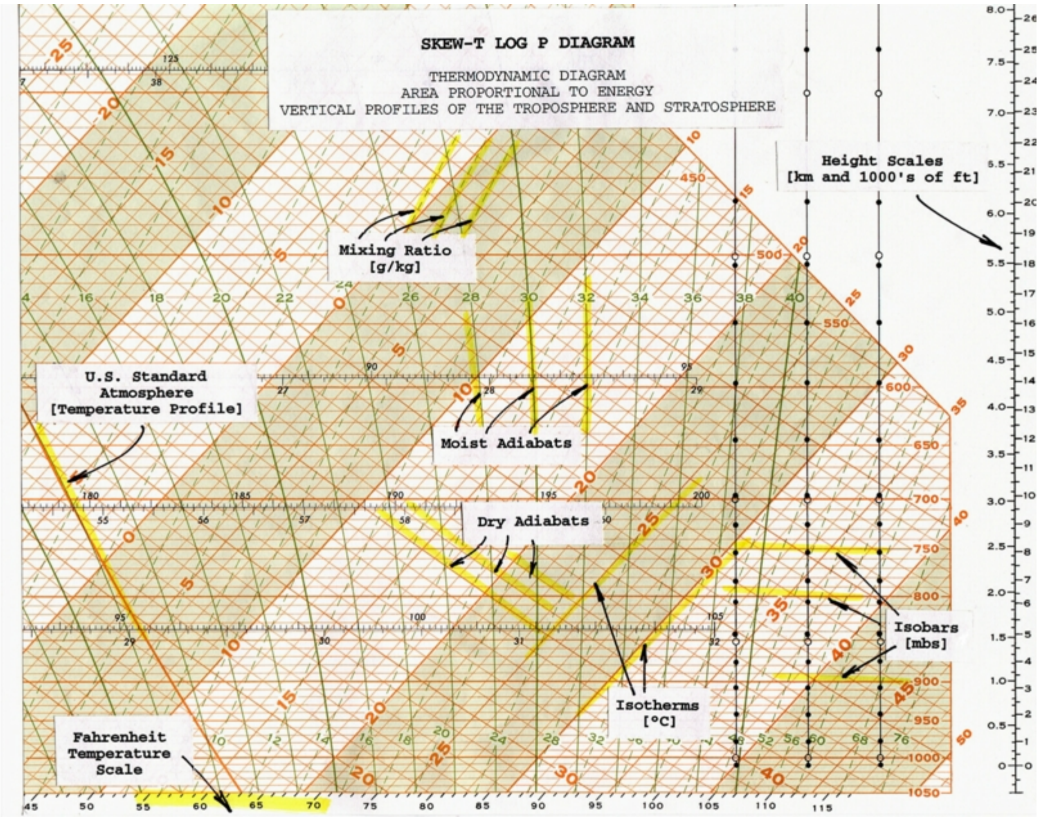

Figure 3: Pielke Blog