Atmospheric Thermodynamics

The Second Law of Thermodynamics and Entropy

The first law of thermodynamics is a statement of conservation of energy.

The second law of thermodynamics is concerned with the maximum fraction of a quantity of heat that can be converted into work.

The Carnot Cycle

Cyclic process - a series of operations by which the state of a substance (called the working substance) changes but the substance is finally returned to its original state in all respects

Work (w) is done by (or on) the working substance if its volume changes.

The internal energy (u) of the working substance is unchanged by the cyclic process, since internal energy is a property of state and the initial and final state are the same.

Then from the first law of thermodynamics:

$$q - w = u_2 - u_1$$

we find:

$$q - w = 0$$
$$q = w$$

The net heat absorbed (q) is equal to the work done (w) during the cyclic process (or cycle).

Reversible transformation - each state of the system is in equilibrium so that a reversal in the direction of an infinitesimal change returns the working substance and the environment to their original states.

Heat engine - a device that does work through the agency of heat.

Consider a cycle of a heat engine in which Q_1 heat is absorbed and Q_2 heat is rejected.
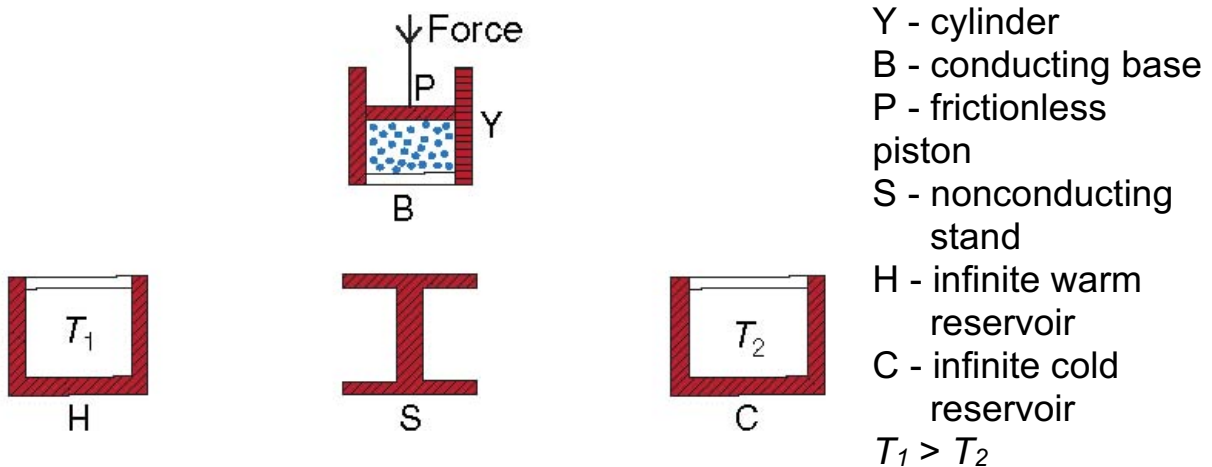
The net heat absorbed is:

$q = Q_1 - Q_2$

and the work (w) done by the engine is:

$$w = q = Q_1 - Q_2$$

The efficiency of the engine (η) is defined as:

$$\eta = \frac{\text{Work done by the engine}}{\text{Heat absorbed by the working substance}} = \frac{w}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

Consider an ideal heat engine as illustrated below:

Y - cylinder
B - conducting base
P - frictionless piston
S - nonconducting stand
H - infinite warm reservoir
C - infinite cold reservoir
$T_1 > T_2$

Heat is supplied to the working substance when the cylinder (Y) is placed on the warm reservoir (H).

Heat is extracted from the working substance when the cylinder (Y) is placed on the cold reservoir (C).

Work is done by the working substance when it expands and the piston (P) is pushed outward.

Work is done on the working substance when the piston (P) pushes inward and the working substance contracts.
Carnot Cycle
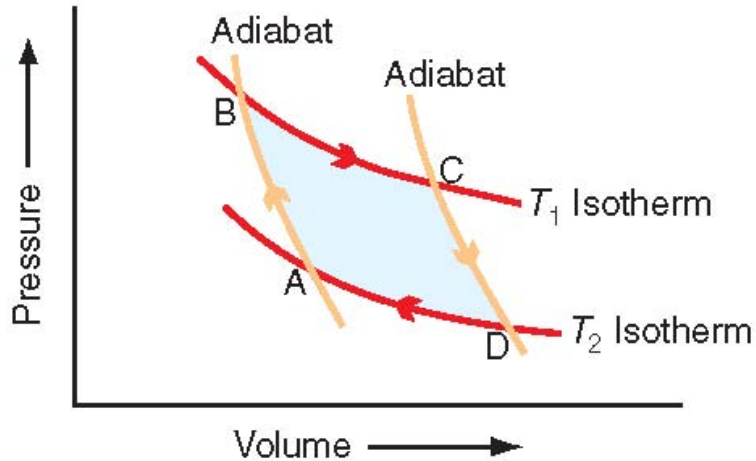
i. Start at point A with $T=T_2$

The cylinder is placed on the stand and the working substance is compressed (move from A to B).

Since the cylinder is on a nonconducting stand no heat is added to or extracted from the working substance, and the compression is adiabatic.

During this adiabatic compression the temperature of the working substance increases to T_1

Why does the temperature increase during this step of the cycle?

ii. The cylinder is placed on the warm reservoir and isothermally expands at temperature T_1. (move from B to C).

During this step the working substance does work (by expanding against the force of the piston) and extracts a quantity of heat (Q_1) from the warm reservoir.

How do we know that the working substance extracts heat during this step?

iii. The cylinder is placed on the nonconducting stand and expands adiabatically (move from C to D).

The temperature decreases from T_1 to T_2.
The working substance does work during this expansion.

How do we know that work is done by the working substance for this transformation?

iv. The cylinder is placed on the cold reservoir and is compressed isothermally (at temperature T_2) back to its original state (move from D to A)

During this isothermal compression the working substance rejects a quantity of heat (Q_2) to the cold reservoir.

How do we know that heat is rejected to the cold reservoir during this step?

The amount of work done during this Carnot cycle is given by:

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

and is given by the area enclosed by ABCD on the p-V diagram.

Since this is a cyclic process, the internal energy of the system is unchanged, and the work done is equal to net heat added to the system (Q_1 - Q_2).

The efficiency of this heat engine is given by:

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

In this process the heat engine did work by transferring heat from the warm reservoir to the cold reservoir.

One statement of the second law of thermodynamics is "only by transferring heat from a warmer to a colder body can heat be converted into work in a cyclic process"

Carnot's theorems

For a given range of temperatures no engine can be more efficient than a reversible engine.

All reversible engines, working between the same range of temperatures, have the same efficiency.

For the Carnot cycle the ratio of heat absorbed (Q_1) to heat rejected (Q_2) is equal to the ratio of the temperature of the warm reservoir (T_1) to the temperature of the cold reservoir (T_2):

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

What are some examples of real heat engines?

What is an atmospheric example of a heat engine?

If the Carnot cycle is run in reverse a quantity of heat (Q_2) is taken from the cold reservoir and a quantity of heat (Q_1) is transferred to the warm reservoir $(Q_1>Q_2)$.

In order for heat to be transferred from the cold to the warm reservoir mechanical work $(=Q_1 - Q_2)$ must be done on the working substance.

What is an example of a reversed heat engine?

Another statement of the second law of thermodynamics is "heat cannot of itself (i.e. without the performance of work by some external agency) pass from a cooler to a warmer body in a cyclic process"

Entropy
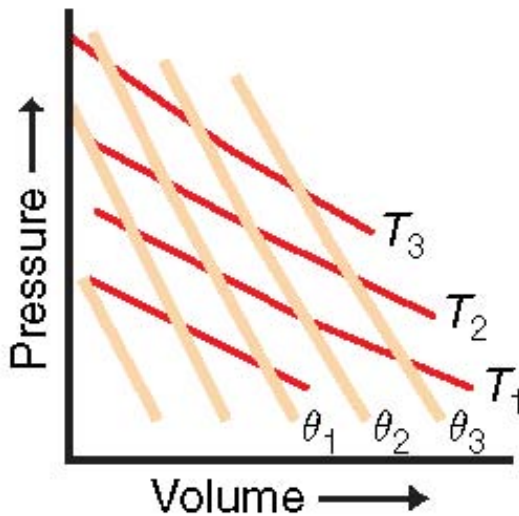
Is heat added to or extracted from the working substance for an isothermal transition from adiabat θ_1 to θ_2?

The heat associated with this transition is Q_{rev}.

If we consider another isothermal transition from adiabat θ_1 to θ_2 at a different temperature the amount of heat associated with the transition will be different but the ratio Q_{rev}/T will be the same.

We can then use Q_{rev}/T as a measure of the difference between the two adiabats, which is referred to as the difference in entropy.

The change in entropy of a system is defined by:

$$dS \equiv \frac{dQ_{rev}}{T}$$

and the change in entropy for a unit mass of a substance is given by:

$$ds \equiv \frac{dq_{rev}}{T}$$

Entropy is a function of state of the system and is independent of the path by which the system is brought to that state.

For the transition of a system from state 1 to state 2:

$$s_2 - s_1 = \int_1^2 \frac{dq_{rev}}{T}$$

Taking the first law of thermodynamics:

$$dq = du + pd\alpha$$

and the definition of entropy gives:

$$Tds = du + pd\alpha$$

which is a form of the first law of thermodynamics that contains only functions of state.

We can relate entropy and potential temperature by taking the first law of thermodynamics expressed as:

$$dq = c_p dT - \alpha dp$$

and rewriting using the equation of state to give:

$$dq = c_p dT - \frac{RT}{p} dp$$

$$\frac{dq}{T} = c_p \frac{dT}{T} - R \frac{dp}{p}$$

Combining this with Poisson's equation expressed as:

$$c_p \frac{d\theta}{\theta} = c_p \frac{dT}{T} - R \frac{dp}{p}$$

gives

$$\frac{dq}{T} = c_p \frac{d\theta}{\theta}$$

$$ds = c_p \frac{d\theta}{\theta}$$

Integrating this equation gives:

$$s = c_p \ln \theta + \text{constant}$$

For an adiabatic process both the potential temperature and the entropy will be constant. This type of process can be referred to as being isentropic (constant entropy).

Similarly, adiabats on a thermodynamic diagram are often referred to as isentropes.

The Carnot cycle can be illustrated on a temperature-entropy diagram:
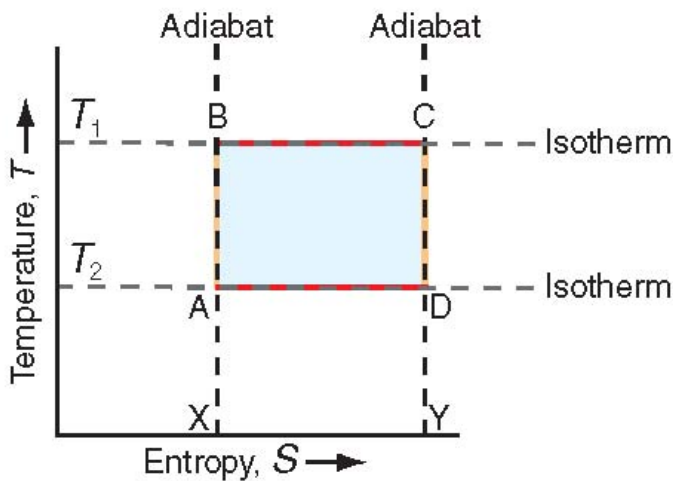
The heat associated with any transition on this diagram is proportional to the area under the curve that represents the transition.

During which steps of the Carnot cycle ABCDA is heat absorbed by (Q_1) or extracted from (Q_2) the working substance?

The difference in heat added to and extracted from the working substance during the Carnot cycle (Q_1-Q_2) is given by the area ABCD and is equal to the work done.

On a skew T – log p chart area is also proportional to net work.

Clausius-Clapeyron Equation

The Clausius-Clapeyron equation relates the change in saturation vapor pressure above a liquid surface to changes in temperature and is an essential equation in atmospheric science.

Derivation of the Clausius-Clapeyron Equation

Take the first law of thermodynamics expressed as:

$dq = du + pd\alpha$

Integrate this equation over the phase transition from liquid (phase 1) to vapor (phase 2):

$$\int_{q_1}^{q_2} dq = \int_{u_1}^{u_2} du + \int_{\alpha_1}^{\alpha_2} pd\alpha = L_v$$

Latent heat of vaporization (L_v): The heat required to convert a unit mass of liquid to vapor at constant temperature and pressure

The constant pressure over which this phase change occurs is the saturation vapor pressure (e_s).

$$L_v = u_2 - u_1 + e_s(\alpha_2 - \alpha_1)$$

Since T is constant for this phase change we can also write:

$$L_v = \int_{q_1}^{q_2} dq = T\int_{q_1}^{q_2} \frac{dq}{T} = T\int_{s_1}^{s_2} ds = T(s_2 - s_1)$$

where we have used the definition of entropy (s).

Equating these two expressions for L_v gives:

$$T(s_2 - s_1) = u_2 - u_1 + e_s(\alpha_2 - \alpha_1)$$
$$u_1 + e_s\alpha_1 - Ts_1 = u_2 + e_s\alpha_2 - Ts_2$$

Gibbs function (G): $G = u + e_s \alpha - Ts$

For a phase change $G_1 = G_2$

Differentiation of G gives:

$$dG = du + e_s d\alpha + \alpha de_s - Tds - sdT$$

From the first law of thermodynamics and the definition of entropy:

$$dq = du + pd\alpha = du + e_s d\alpha = Tds$$

Using this expression in the equation for dG gives:

$$dG = \alpha de_s - sdT$$

Since $G_1 = G_2$ and $dG_1 = dG_2$ then

$$dG_1 = \alpha_1 de_s - s_1 dT = \alpha_2 de_s - s_2 dT = dG_2$$

$$\alpha_1 de_s - \alpha_2 de_s = s_1 dT - s_2 dT$$
$$de_s(\alpha_1 - \alpha_2) = dT(s_1 - s_2)$$
$$\frac{de_s}{dT} = \frac{(s_1 - s_2)}{(\alpha_1 - \alpha_2)} = \frac{(s_2 - s_1)}{(\alpha_2 - \alpha_1)}$$

Noting that:

$$(s_2 - s_1) = ds = \frac{dq}{T} = \frac{L_v}{T}$$

gives

$$\frac{de_s}{dT} = \frac{L_v}{T(\alpha_2 - \alpha_1)}$$

which is the Clausius-Clapeyron equation.

In the atmosphere $\alpha_2 \gg \alpha_1$ (the specific volume of water vapor $\gg$ the specific volume of liquid water) and using the equation of state for water vapor allows us to write the Clausius-Clapeyron equation as:

$$\frac{de_s}{dT} \approx \frac{L_v}{T\alpha_2} = \frac{L_v e_s}{R_v T^2}$$

We can then use this equation to determine changes in e_s as T varies, by integrating this equation, while assuming that L_v is constant:

$$\int_{e_{s0}(T_0)}^{e_s(T)} \frac{de_s}{e_s} = \int_{T_0}^{T} \frac{L_v}{R_v T^2} dT$$

$$\ln\left(\frac{e_s}{e_{s0}}\right) = -\frac{L_v}{R_v}\left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{L_v}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

$$e_s(T) = e_{s0} \exp\left[\frac{L}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$$

where e_{s0} is the known saturation vapor pressure at temperature T_0.

e_{s0} can be determined experimentally, and for $T_0 = 0$ deg C $e_{s0} = 611$ Pa

Also at $T_0 = 0$ deg C = 273.15 K $L_v = 2.50 \times 10^6$ J kg^{-1}

Using these values of L_v, T_0, and e_{s0} gives:

$$e_s(T) = A \exp\left[\frac{-B}{T}\right],$$

where:

$$A = e_{s0} \exp\left[\frac{L_v}{R_v T_0}\right] = 2.56 \times 10^{11} \text{ Pa}$$

$$B = \frac{L_v}{R_v} = 5.42 \times 10^3 \text{ K}$$

Calculate the saturation vapor pressure at the ATOC weather station at SEEC.

As the air temperature increases the amount of water vapor required for the air to become saturated increases at an exponential rate.

Similarly, as air is cooled the amount of water vapor required for the air to become saturated decreases at an exponential rate.

The derivation of the Clausius-Clapeyron equation given above assumed that L_v was constant, but in fact L_v varies with T.

From our derivation of the Clausius-Clapeyron equation we know:

$$L_v = u_2 - u_1 + e_s(\alpha_2 - \alpha_1)$$

and $\alpha_2 >> \alpha_1$, so

$$L_v \approx u_2 - u_1 + e_s\alpha_2$$

Using the equation of state for water vapor ($e_s\alpha_2 = R_vT$) gives:

$$L_v = u_2 - u_1 + R_vT$$

Taking the derivative of L_v with respect to T gives:

$$\frac{dL_v}{dT} = \frac{du_2}{dT} - \frac{du_1}{dT} + R_v$$

Noting that $c_v = \dfrac{du}{dT}$, so

$$\frac{du_2}{dT} = c_{vv}$$

Specific heat of water vapor at constant volume: c_{vv} = 1410 J kg^{-1} K^{-1}

$$\frac{du_1}{dT} = c$$

Specific heat of water: c = 4187 J kg^{-1} K^{-1}

Also $c_{pv} = c_{vv} + R_v$ = 1870 J kg^{-1} K^{-1}, so:

$$\frac{dL_v}{dT} = c_{vv} - c + R_v = c_{pv} - c$$

Taking c_{pv} and c as constants we can integrate this equation to find $L_v(T)$:

$$\int_{L_{v0}(T_0)}^{L_v(T)} dL_v = \int_{T_0}^{T} \left(c_{pv} - c\right) dT$$

$$L_v(T) - L_{v0}(T_0) = \left(c_{pv} - c\right)(T - T_0)$$

$$L_v(T) = L_{v0}(T_0) + \left(c_{pv} - c\right)(T - T_0)$$

This expression for $L_v(T)$ can be used when integrating the Clausius-Clapeyron equation to give a more accurate value for e_s.

In addition, the specific heats of water vapor and liquid water are also functions of T, and this can also be taken into account when integrating the Clausius-Clapeyron equation.

These more exact values of e_s are given below:

TABLE 2.1. *Saturation Vapor Pressures Over Water and Ice,*
and Latent Heats of Condensation and Sublimation

T (°C)	e_s (Pa)	e_i (Pa)	L (J/g)	L_s (J/g)
−40	19.05	12.85	2603	2839
−35	31.54	22.36		
−30	51.06	38.02	2575	2839
−25	80.90	63.30		
−20	125.63	103.28	2549	2838
−15	191.44	165.32		
−10	286.57	259.92	2525	2837
−5	421.84	401.78		
0	611.21	611.15	2501	2834
5	872.47		2489	
10	1227.94		2477	
15	1705.32		2466	
20	2338.54		2453	
25	3168.74		2442	
30	4245.20		2430	
35	5626.45		2418	
40	7381.27		2406	

Example: Using the equation for $L_v(T)$ calculate the latent heat of vaporization for T = 30 deg C

An empirical formula fit to the saturation vapor pressure data in the table is:

$$e_s = e_0 \exp\left(\frac{b(T - T_1)}{T - T_2}\right) \quad \text{(units: hPa)}$$

e_0 = 6.112 hPa
b = 17.67
T_1 = 273.15 K
T_2 = 29.65 K

The dew point temperature (T_d) can be used with the Clausius-Clapeyron equation to calculate the vapor pressure (e) with:

$$e = e_0 \exp\left(\frac{b(T_d - T_1)}{T_d - T_2}\right) \text{ (units: hPa)}$$

The constants e_0, b, T_1, and T_2 are the same as those used when calculating e_s from T.

Example: Calculate the vapor pressure, saturation vapor pressure, and relative humidity from the observed T, T_d, and p at the ATOC weather station.

Using the Clausius-Clapeyron equation and the relationship between the humidity variables discussed earlier we can convert between any of the following variables:

Actual Moisture Content	Saturated Moisture Content
T_d	T
e	e_s
w	w_s
q	q_s

Saturation vapor pressure over an ice surface (e_{si})

The saturation vapor pressure over an ice surface can be calculated from the Clausius-Clapeyron equation by replacing L_v, the latent heat of vaporization, with L_s, the latent heat of sublimation.

Latent heat of sublimation (L_s): The heat required to convert a unit mass of ice to vapor at constant temperature and pressure (= 2.85×10^6 J kg^{-1} K^{-1})

The saturation vapor pressure over an ice surface is given by:

$$e_{si} = e_{si0} \exp\left[\frac{L_s}{R_v}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right],$$

$$e_{si} = A_i \exp\left[\frac{-B_i}{T}\right]$$

where

$$A_i = e_{si0} \exp\left[\frac{L_s}{R_v T_0}\right] = 4.13 \times 10^{12} \text{ Pa}$$

$$B = \frac{L_s}{R_v} = 6.18 \times 10^3 \text{ K}$$

Combining the expressions for e_s and e_{si} gives:

$$\frac{e_s(T)}{e_{si}(T)} = \exp\left[\frac{L_f}{R_v T_0}\left(\frac{T_0}{T} - 1\right)\right]$$

where L_f is the latent heat of fusion (=3.34×10^5 J kg^{-1})

Generalized Statement of the Second Law of Thermodynamics

The first part of the second law of thermodynamics states:

for a reversible transformation there is no change in the entropy of the universe (where universe refers to a system and its surroundings).

Therefore if a system receives heat reversibly the increase in its entropy is exactly equal to the decrease in entropy of the surroundings.

In reality all natural transformations are irreversible to some extent.

For an irreversible transformation:

$$ds \neq \frac{dq_{irrev}}{T}$$

and there is no simple relationship between the change in entropy of the system and the change in entropy of its surroundings.

The second part of the second law of thermodynamics states:

the entropy of the universe increases as a result of irreversible transformations

The second law of thermodynamics can then be summarized by:

$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

$\Delta S_{universe} = 0$ for reversible (equilibrium) transformations

$\Delta S_{universe} > 0$ for irreversible (spontaneous) transformations

In general entropy is a measure of the degree of disorder (randomness) of a system.

Therefore irreversible transformations increase the randomness of the universe.