Review of Thermodynamics (continued)

Topics:
- Second law of thermodynamics
- Derivation of the Clausius-Clapeyron equation
- Saturation vapor pressure

Second Law of Thermodynamics

The first law is a statement about energy conservation, but the second law tells us which out of many conceivable processes that conserve energy are possible and which are not. An example would be the idea to extract some of the internal energy from the ocean and convert it completely to useful work.

There are many statements of the second law:

Clausius: “It is impossible for any self-acting machine to convey heat continuously from a body at a given temperature to another body at a higher temperature.”

Lord Kelvin: “A transformation in which the only final result is to transform heat extracted from some source at a uniform temperature, T, completely into work, is impossible.”

Wallace and Hobbs: “Only by transferring heat from a warmer body to a colder body can that heat be converted into work in a cyclic process.”

“Energy flows from a warm body to a cold body.”

The second law is often stated in terms of entropy, s (in this case, per unit mass)

\[ ds = \frac{dq_{\text{reversible}}}{T} . \]  

(1)

Note that entropy is a function of state and not of path.

Combining Equation 1 with the first law gives

\[ Tds = c_p dT - \alpha dp . \]

Entropy is related to potential temperature in an important way. We use the equation of state to substitute for \( \alpha \), and divide through by \( T \) to produce
The RHS looks quite similar to terms in our derivation of potential temperature. Begin with the definition of potential temperature

$$\theta = T \left( \frac{p_0}{p} \right)^{R/c_p}.$$ 

Taking the natural log of both sides, differentiating, and slightly rearranging terms gives

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

the RHS of which happens to match the RHS of Equation 2. So

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

and integrating,

$$s = c_p \ln \theta + \text{const.} \quad (3)$$

Equation 3 tells us that a constant potential temperature process is a constant entropy process. Lines of constant $\theta$ on a thermodynamic chart (or isopleths of $\theta$ on a map) are line so constant entropy.

Transformations for which entropy remains constant are called isentropic.

**Derivation of the Clausius-Clapeyron Equation**

The equation of state for water vapor is

$$e = \rho_v R_v T,$$

where $R_v$ is the gas constant for water vapor (461.5 J K$^{-1}$ kg$^{-1}$).

Consider an sealed, thermally insulated box partially filled with water as shown in the figure.

![Diagram](image)

The population of molecules in the liquid phase is characterized by a distribution of kinetic energies, some greater and some less. We can imagine some of the higher-KE molecules breaking away from the liquid into the vapor phase. Lower-KE molecules in the vapor phase, similarly, collide with the surface and become liquid phase.
For a fixed temperature, equilibrium will eventually be reached, when the number of liquid molecules transforming to vapor are equal to the number of vapor molecules becoming liquid. This equilibrium condition is called *saturation*, and the vapor pressure is called the saturation vapor pressure. The saturation vapor pressure is dependent on temperature alone, which will now be demonstrated.

Changing phase from liquid to vapor requires energy, since the KE of vapor molecules is greater than KE of liquid molecules. For the transition from liquid phase (1) to vapor phase (2), we integrate the first law, 

\[ \int_{s_1}^{s_2} T ds = \int_{u_1}^{u_2} du + \int_{\alpha_1}^{\alpha_2} p d\alpha, \] (4)

where the LHS, the heat required to convert a unit of mass of liquid into water vapor, can be denoted by \( L \).

For the isothermal and isobaric phase change process, Equation 4 becomes 

\[ T(s_2 - s_1) = u_2 - u_1 + e_s(\alpha_2 - \alpha_1), \]

where \( L = T(s_2 - s_1) \).

Rearranging, 

\[ u_1 + e_s \alpha_1 - Ts_1 = u_2 + e_s \alpha_2 - Ts_2. \]

The thermodynamic quantity \( u + p\alpha - Ts \) is called the Gibbs function and is denoted by \( G \). [Note that \( G \) is per unit mass and that using the capital letter is inconsistent with our previous convention. However, we wouldn’t want to confuse it with \( g \), now would we?]

What’s the use of yet another thermodynamic parameter, especially one that is not conserved under changes of temperature or pressure? \( G \) is useful for evaluating transformations of phase, which occur under isothermal and isobaric conditions.

Differentiating \( G \) produces 

\[ dG = du + e_s d\alpha + \alpha de_s - Tds - sdT. \] (5)

From Equation 4, we know that \( Tds = du + e_s d\alpha \), which substituting into Equation 5 gives 

\[ dG = \alpha de_s - sdT. \]

Since the Gibbs free energies for liquid and vapor phases, \( dG_1 = dG_2 \) and 

\[ \alpha_1 de_s - s_1dT = \alpha_2 de_s - s_2dT, \]

which can be simplified to give the Clausius-Clapeyron equation,
Because density of liquid water is three orders of magnitude greater than the typical atmospheric vapor density, \( \alpha_2 \gg \alpha_1 \). Assuming this and using the equation of state for water vapor, Equation 6 becomes

\[
\frac{de_s}{dT} = \frac{s_2 - s_1}{\alpha_2 - \alpha_1} = \frac{L}{T(\alpha_2 - \alpha_1)}.
\]  

Equation 7 can be integrated to solve for the dependence of \( e_s \) on temperature,

\[
e_s = e_{s0}\exp\left\{\frac{L}{RT_0}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\}.
\]  

At 0 °C, \( e_s = 6.11 \) mb.

A similar development can be made for saturation vapor pressure over ice.

The assumption of constant \( L \) in integrating Equation 7 leads to unacceptable errors in some circumstances. A better saturation vapor pressure relation to use is the empirical formula from Bolton (1980 Monthly Weather Review),

\[
e_s = 6.112\exp\left(\frac{17.67T}{T + 243.5}\right),
\]

where \( T \) is in °C and \( e_s \) is in mb.