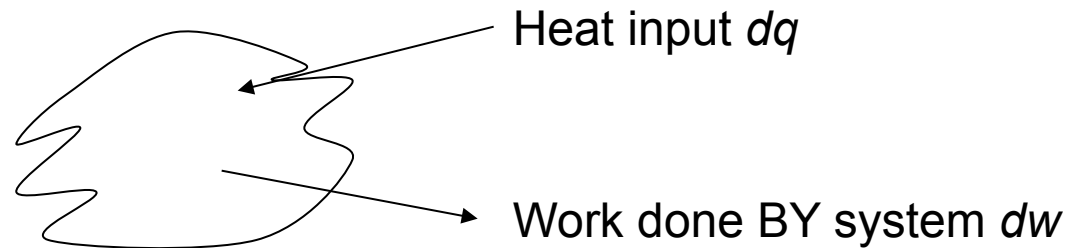


THE FIRST LAW of THERMODYNAMICS: *Conservation of energy*



If we identify du as the change in internal energy of the system (associated with changes in the kinetic and potential energy of the molecules), we write

The “First Law” of Thermodynamics as: $dq = du + dw$

If the work is mechanical work (expansion work), as we defined last time, then we can write $dw = pdv$, and

$$dq = du + pdv$$

Internal energy is a STATE VARIABLE: the change in internal energy is the difference between initial and final *states*. du is **independent of path between initial and final states**.

The state variables, like u , are functions of any TWO independent intensive variables, e.g., p , T , v (*specific volume*). E.g., we can express $u = u(v, T)$.

JOULE'S LAW: Joule's experiment (a thought experiment here) demonstrated that, **for an Ideal Gas**, the internal energy u is a function of T only. Let's see how to show this:

Consider a gas expanding into an evacuated cylinder (vacuum). Since p is zero, no mechanical work is done and $dw = 0$.

Imagine that the process is also adiabatic (perfectly insulated walls), so $dq = 0$.

Since $dq = dw = 0$, $du = 0$.

Under these conditions, it's clear that the volume of the gas changed, as did the potential energy of the molecular configuration. Therefore the internal energy of the gas must be independent of volume, and is only a function of T .

Joule showed experimentally that the temperature of the gas in such an experiment remained constant.

Joule's Law states: "if a gas expands without doing any work, and under adiabatic conditions, the temperature of the gas remains constant."

Corollary: Molecules of an ideal gas do not exert any attractive or repulsive forces on one another.

Specific Heats and Heat Capacities

Specific heat and heat capacities for various substances allow for T changes to be calculated per unit of heat added to the substance.

If heat is added to a substance at constant pressure, we define the specific heat at constant pressure, c_p , as

$$c_p = \left(\frac{\partial q}{\partial T} \right)_p$$

(*aside: $m C_p$ is the HEAT CAPACITY – unit difference*)

If volume remains constant during heating, we define the specific heat at constant volume, c_v , as

$$c_v = \left(\frac{\partial q}{\partial T} \right)_v$$

If we know what values these properties have for ideal gases, then we can readily compute temperature changes that occur under addition of heat.

We'll start by deriving equivalent forms of the First Law for ideal gases that are easier to work with.

Start with the definition of c_v : $c_v = \left(\frac{\partial q}{\partial T} \right)_v$

But if $dv = 0$ then $dw = 0$, and the First Law reduces to $dq = du$

Therefore $c_v = \left(\frac{\partial u}{\partial T} \right)_v$

If we consider an **Ideal Gas**, u depends only upon T .
Therefore the restriction on constant volume can be dropped, and

$$c_v = \frac{du}{dT} \quad (\text{generally true})$$

Use $p\alpha = RT$

(Please note v and α denote same thing)

First Law can then be written as $dq = c_v dT + p d\alpha$

Express the last term differently: $dq = c_v dT + d(p\alpha) - \alpha dp$
 $= c_v dT + R dT - \alpha dp$
 $= (c_v + R) dT - \alpha dp$

At constant **pressure**, $\alpha dp = 0$ and equation becomes $dq = (c_v + R) dT$

Since $c_p = \left(\frac{\partial q}{\partial T} \right)_p$, we see $c_p = c_v + R$ \implies $dq = c_p dT - \alpha dp$

Equivalent form of first law for an ideal gas

Since $c_p = c_v + R$; $c_p > c_v$

In a constant pressure process, volume expands, and hence some of the heat added goes into expanding the volume instead of increasing T

$$dT = \frac{dq}{c_v} \text{ or } \frac{dq}{c_p}$$

For dry air; $c_v = 717 \text{ J deg}^{-1} \text{ kg}^{-1}$
 $c_p = 717 + 287 = 1004 \text{ J deg}^{-1} \text{ kg}^{-1}$

Where did those values come from? (let's see how c_p and c_v values are derived).

From statistical mechanics, $u = \frac{1}{2}kT$ = $\frac{1}{2}RT$ which is an expression for the
per molecule per mole

Internal Energy per degree of freedom. (This expression is valid as far as $kT \ll$ electronic excitation levels ($<10^4$ °K)).

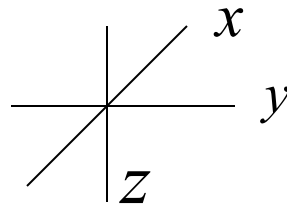
For **monatomic gases** we have 3 degrees of freedom associated with x,y,z direction velocities. Hence

$$u = \frac{3}{2}RT \quad \text{Hence } c_v = \frac{3}{2}R \text{ (per unit mass), since } c_v = \frac{du}{dT}$$

Also, since

$$c_p = c_v + R \text{ we have } c_p = \frac{5}{2}R$$

For **diatomic molecules**, more closely representative of air (e.g. O₂, N₂), we have higher order degrees of freedom. Consider the following model,



a diatomic molecule is oriented along the y-axis

- This molecule has 3 degrees of freedom for translational motion and 2 rotational modes (x,z axes)
- The moments of inertia around the x & z axes are very much larger than the moments of inertia around the y-axis.
- The molecule also has 2 vibrational modes (position & velocity) but the vibrational modes are usually dominated by the rotational modes for atmospheric (troposphere/stratosphere) temperatures. Thus,

$$u = \frac{5}{2}RT \quad \text{so} \quad c_v = \frac{5}{2}R \quad \text{and} \quad c_p = \frac{7}{2}R$$

Therefore for dry air (modeled as an ideal, diatomic gas) we can estimate

$$c_v = \frac{5}{2}R_d = \frac{5}{2}(287.05J \text{ deg}^{-1} \text{ kg}^{-1}) = 717J \text{ deg}^{-1} \text{ kg}^{-1}$$

$$c_p = \frac{7}{2}R_d = 1004J \text{ deg}^{-1} \text{ kg}^{-1}$$

(Note units) 6

Quick Summary thus far:

- The First Law is $du = dq - dw$
- Heat capacities are *defined* as partial derivatives of q with respect to T , at constant v OR p .
- The internal energy of an ideal gas is a function of temperature only, so the following is always true:

$$du = c_v dT$$

- For an ideal gas, we can then write the First Law as either

$$dq = c_v dT + pdv$$

$$dq = c_p dT - vdp$$

- c_p and c_v can be found theoretically for monatomic and diatomic gases
- So we can compute T changes (and thus internal energy changes, since they depend only on T !) if we know the heat in/out and dv or dp changes

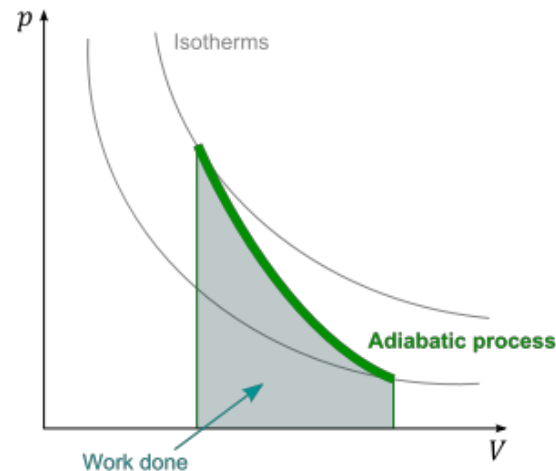
ADIABATIC PROCESSES

An **adiabatic process** involves no heat exchange between a substance & its surroundings. Hence $dq = 0$

Therefore, for an adiabatic transformation, $dw = -du = c_v dT$

→ Work done is equal to the decrease in internal energy

In this example two different paths are used to go from V_1 to V_2 .



$$PV = nRT$$

http://en.wikipedia.org/wiki/Adiabatic_process

Notice that the adiabat is drawn steeper than the isotherm. Why?

During the adiabatic compression $dq = 0$ and $p dv < 0$ (volume decreases)

To obey the First Law ($du=dw$), T must increase. In contrast, T remains constant during the isothermal compression. Since the final temperature is higher in the adiabatic compression, therefore (by Ideal Gas Law), final P must also be higher than for isothermal process: So adiabat is steeper than isotherm.

The Adiabatic Air Parcel

Idealized model of an air parcel is a small volume of air:

- Thermally insulated from the environment so temperature changes are adiabatic
- Parcel pressure immediately adjusts to environmental pressure
- Parcel moves slowly enough such that macroscopic KE is negligible portion of total energy

Consider such a parcel moving about under adiabatic conditions

What is the change in temperature with height?

Use First Law and assume Ideal Gas:

~~$$dq = du + dw$$~~

We chose this form over

$$0 = c_p dT - \frac{1}{\rho} dp$$

$$0 = c_p dT - \alpha dp$$

$$dq = c_v dT + p d\alpha$$

or

$$c_p dT = -g dz$$

using the hydrostatic equation

$$\frac{dp}{dz} = -\rho g$$

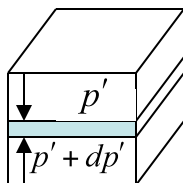
$$\frac{dT}{dz} = \frac{-g}{c_p} \equiv T_d$$

$$T_d = 9.8^\circ C / km$$

Dry adiabatic lapse rate

In the above derivation we used the hydrostatic equation

-Derivation



$$p' + dp = p' - \rho g dz$$

(force balance)

The Potential Temperature: Of fundamental importance to adiabatic processes in the atmosphere is the concept of potential temperature, θ

Again use the First Law for an adiabatic process,

$$0 = c_p dT - \frac{RT}{p} dp \qquad 0 = c_p dT - \alpha dp$$

$$\qquad \qquad \qquad p\alpha = RT$$

or

$$\frac{c_p}{R} \frac{dT}{T} - \frac{dp}{p} = 0$$

Integrating from P_o where $T = \theta$ to some point P, T

$$\frac{c_p}{R} \int_{\theta}^T d \ln T = \int_{P_o}^P d \ln P$$

which yields, $\theta = T \left(\frac{P_o}{P} \right)^{R/c_p}$ **Poisson's Equation**

θ is the temperature a parcel would acquire if it ascended or descended adiabatically from pressure P to P_o .

(e.g., choose $P_o = 1000mb$)

$$\frac{R}{c_p} = \frac{287 J \text{ deg}^{-1} \text{ kg}^{-1}}{1004 J \text{ deg}^{-1} \text{ kg}^{-1}} = 0.286$$

We expect potential temperature to be **conserved** for (**dry**) adiabatic transformations. As the parcel moves about in the atmosphere under adiabatic conditions, **its potential temperature θ does not change**

Using potential temperature

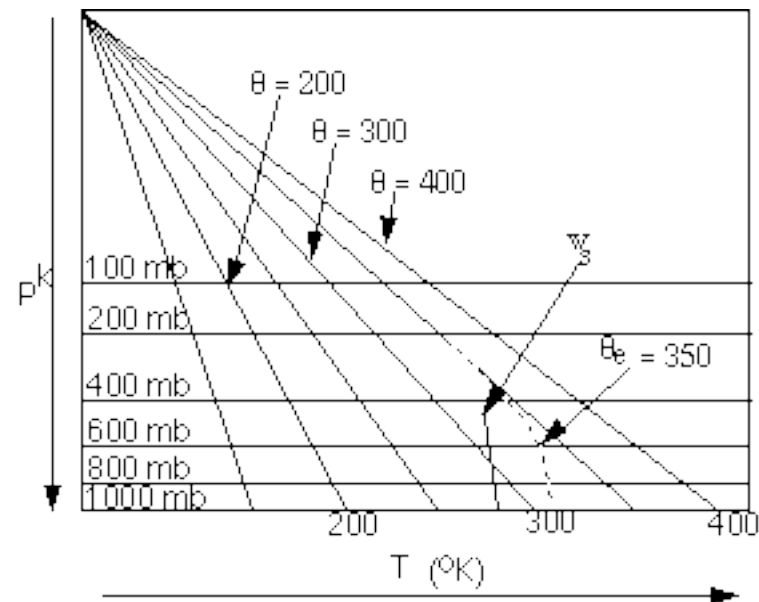
- For an adiabatic process,

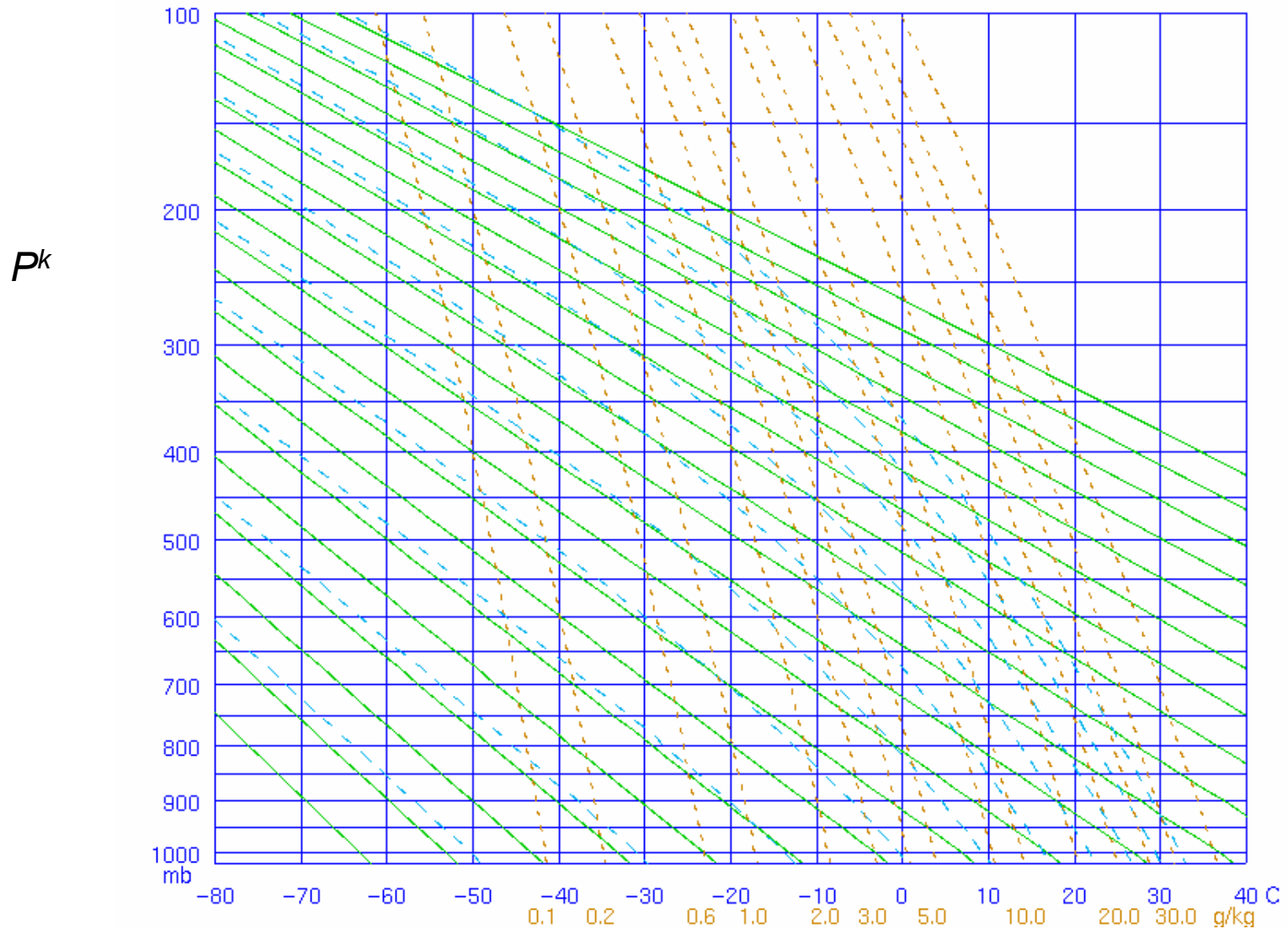
$$c_p dT = \alpha dP = RT \frac{dP}{P}$$

$$\left(\frac{T}{T_0}\right) = \left(\frac{P}{P_0}\right)^k \quad \text{and} \quad \left(\frac{T}{\theta}\right) = \left(\frac{P}{1000 \text{ mbar}}\right)^k$$

$$k = \frac{R}{c_p} = \frac{(c_p - c_v)}{c_p} = 0.286$$

- θ is the temperature that a parcel of air would have if, starting with temperature T and pressure P , it were moved to a final pressure of 1000 mbar
- θ is conserved in an adiabatic process
- Lines of constant θ are also lines of constant entropy (isentropes).
- Stüve diagram (1927): Notice from eqn, for a chosen θ , T varies as P^k
 - Constant- θ lines are straight (solid) lines if we choose the axes properly*
 - Which are isobars, isotherms?*





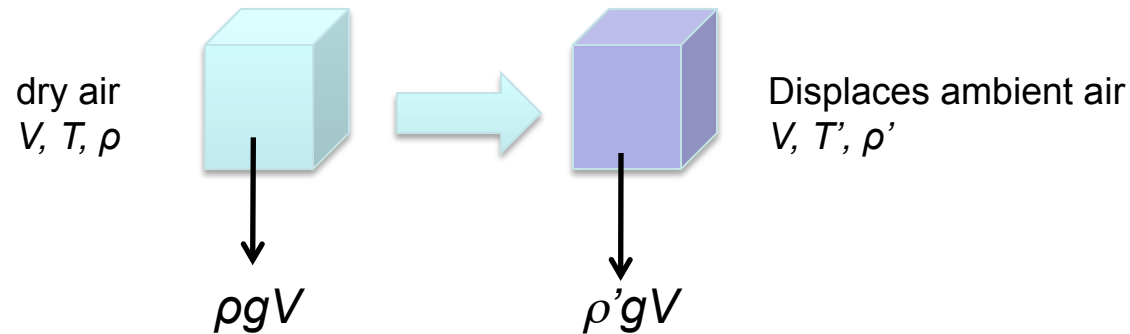
T

Extension: atmospheric stability

We already saw that the dry adiabatic lapse rate is

$$\frac{dT}{dz} = -\frac{g}{c_p} \equiv \Gamma = 0.98^\circ\text{C}/100\text{m}$$

What is the buoyant force on a parcel of air? Net buoyant force upward is $Vg(\rho' - \rho)$



Acceleration of the parcel is equal to the sum of the forces -- here, only buoyancy, so:

$$\frac{d^2z}{dt^2} = g \left(\frac{\rho' - \rho}{\rho} \right) = g \left(\frac{T - T'}{T'} \right)$$

If parcel is warmer than ambient air ($T > T'$), force is positive and parcel moves upward

A dry parcel that starts at temperature T and is lifted Δz has a new temperature $T - \Gamma \Delta z$

Let's suppose the environmental T changes with height at a different rate, so the ambient temperature is $T - \gamma \Delta z$. The excess temperature of the parcel over ambient air is $\Delta z (\gamma - \Gamma)$

Atmospheric stability, continued

When Δz ($\gamma - \Gamma$) is positive, the parcel is warmer than its surroundings and is accelerated upward (unstable atmosphere); if the opposite, a restoring force acts against the direction of any motion (stable atmosphere); if the atmosphere is neutral, its lapse rate is the dry adiabatic lapse rate

In terms of θ

$$dT = \frac{T}{\theta} d\theta + \frac{kT}{P} dP$$

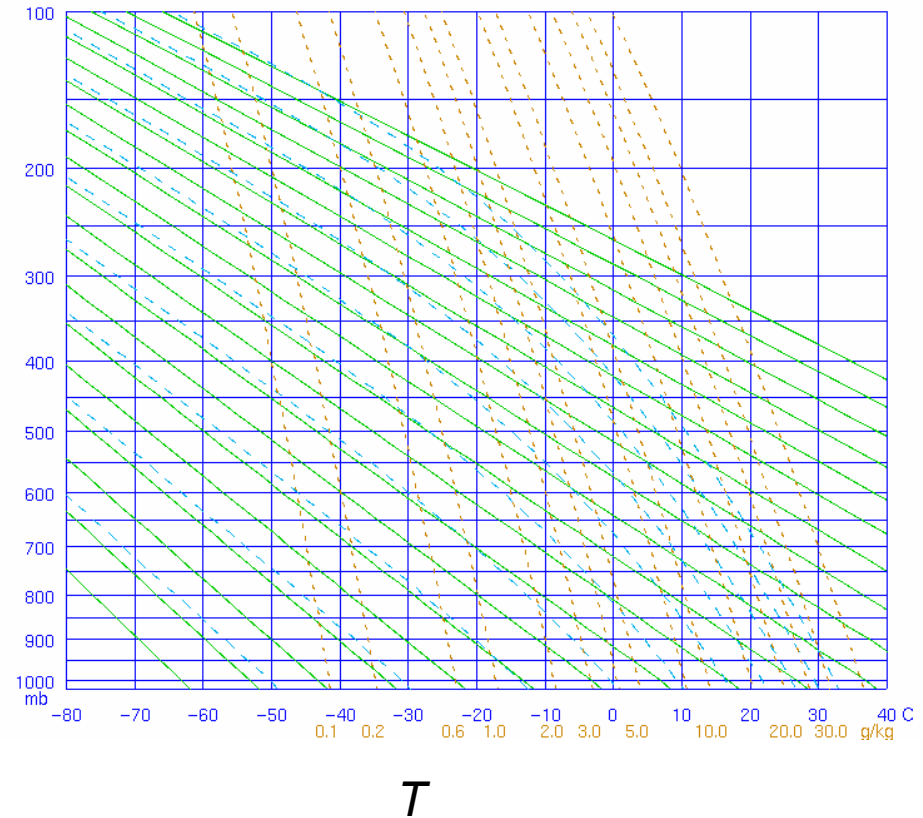
$$\frac{1}{\theta} \frac{\partial \theta}{\partial z} = \frac{1}{T} \frac{\partial T}{\partial z} - \frac{k}{P} \frac{\partial P}{\partial z} = \frac{1}{T} (\Gamma - \gamma)$$

$$\frac{\partial \theta}{\partial z} > 0 \quad \text{stable}$$

$$\frac{\partial \theta}{\partial z} = 0 \quad \text{neutral}$$

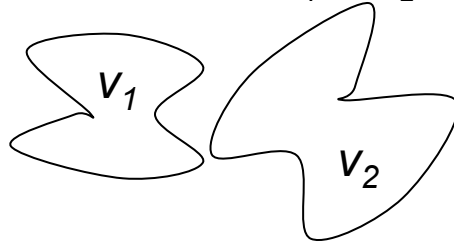
$$\frac{\partial \theta}{\partial z} < 0 \quad \text{unstable}$$

P^k



Other State Variables: Enthalpy

Consider the addition of heat to a substance *at constant pressure* so that the specific volume increases from v_1 to v_2 ; the work done is $p(v_2 - v_1)$



Still assuming constant p so work can be written this way

From First Law,
$$\begin{aligned} dq &= (u_2 - u_1) + p(v_2 - v_1) \\ &= (u_2 + pv_2) - (u_1 + pv_1) \\ &= h_2 - h_1 \end{aligned}$$
 Specific quantities are used here

where $\mathbf{h = u + pv}$ → **definition** of ENTHALPY

For constant pressure process, $dq = dh = h_2 - h_1$ that is, the change in enthalpy is equal to the heat added (or heat extracted).

$dh = du + d(p\alpha)$ ← Complete derivative (α is the same as v above)

$= du + p d\alpha + \alpha dp$

$= dq + \alpha dp$ ($du = dq - p d\alpha$)

$= dq$ when $dp = 0$

Units of $h \rightarrow J kg^{-1}$ or $J mole^{-1}$

$dq = c_p dT - \cancel{\alpha dp}$

$(\alpha dp = 0)$

$dq = dh = c_p dT$

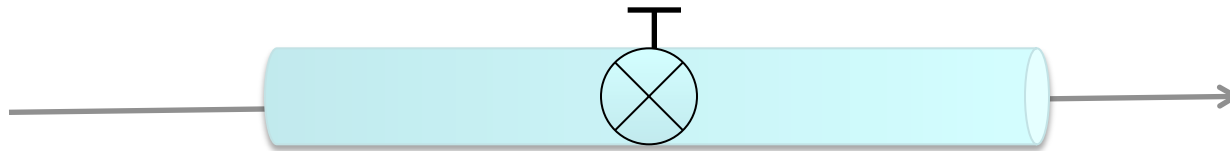
Enthalpy is useful for studying processes at constant pressure, and *open* systems.

Since $h = u + Pv$ and, for an ideal gas, $Pv = RT$, then for the ideal gas $h = u + RT$

R is constant, and $u = u(T)$ only, so we conclude $h = h(T)$ only for an ideal gas.

Aside: application of enthalpy balance in steady-flow system:

energy balance for a single-stream, **steady-flow system** with negligible changes in kinetic and potential energies: $q - w_s = \Delta h$, where w_s is **shaft work**



In the system shown (flow through a “throttling valve”), **the pressure drops across the valve, but no shaft work is done.** The flow through the valve is also **adiabatic**, since there is not much time or area for heat transfer. So we conclude $\Delta h = 0$ and such a valve is an “isenthalpic device” (internal and flow energies are interconverted).

$$dh = 0 = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP$$

From $h = h(T,P)$, taking total derivative

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad \text{and using a Maxwell relation}$$

$$-\frac{1}{c_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] = \left(\frac{\partial T}{\partial P} \right)_h \quad \text{“Joule-Thompson coefficient”, } = 0 \text{ for an ideal gas (show...)}$$

The J-T effect is applied in the *Linde technique*, where the cooling effect is used to liquefy gases, and also in many cryogenic applications (e.g. for the production of liquid oxygen, nitrogen, and argon).

The Second Law of Thermodynamics

(http://en.wikipedia.org/wiki/Second_law_of_thermodynamics)

Clausius' version:

No process is possible whose sole result is the transfer of heat from a body of lower temperature to a body of higher temperature

The second law of thermodynamics is an expression of the **tendency that over time, differences in temperature, pressure, and chemical potential equilibrate in an isolated physical system**. From the state of thermodynamic equilibrium, the law deduced the principle of the increase of entropy and explains the phenomenon of irreversibility in nature. The second law declares the impossibility of machines that generate usable energy from the abundant internal energy of nature by processes called perpetual motion of the second kind.

In classical thermodynamics, the second law is a basic postulate applicable to any system involving measurable heat transfer, and defines the concept of thermodynamic entropy.

The Second Law and Cyclic Processes

The Second Law deals with the maximum amount, or fraction of, heat that can be converted to “work”. For any thermodynamic system there is a theoretical limit to the conversion factor between heat & work.

To study this process further – consider the CARNOT CYCLE (a cyclic process)

CYCLIC PROCESS – a series of change in the state of a substance in which its volume changes and it does work, with the substance returning to its original state. Initial & final state are identical in a cyclic process.

Since the initial & final states are the same, $du = 0$ for a cyclic process.

Therefore $dq = dw$ for a cyclic process.

This implies  **Net work done in a cyclic process is equal to the heat added to the system.**

Consider the following “heat engine”

Input Heat Q_1 \longrightarrow Engine \longrightarrow Q_2 Exhaust Heat

The “efficiency” of this heat engine η is defined as

$$\eta = \frac{\text{workdone}}{\text{heatinput}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

If $Q_2 = 0$ then obviously $\eta = 1$

A “perfect” engine

CARNOT CYCLE

