## **Thermodynamic Properties**

- Define and articulate some of the critical language and concepts of Thermodynamics
- ◦ Distinguish between the universe, system, surroundings, and boundary [Ch 1.1-1.2]
- ◦ Define open system, closed system, and isolated system [Ch 1.1-1.2]
- ◦ Define adiabatic, isothermal, isobaric, and isochoric processes [Ch 1.1-1.2]
- ◦ Distinguish between extensive and intensive thermodynamic properties [Ch 1.3]
- ◦ Explain the difference between state and path variables [Ch 1.5]
- ◦ Distinguish between equilibrium and steady state [Ch 1.4]
- ◦ Define the term phase and explain what it means for phases to be in equilibrium [Ch 1.4]
- Relate properties to phase behavior [Ch 1.6-1.8]
- ◦ Relate the measured thermodynamic properties of temperature and pressure to molecular behavior
- ◦ Describe phase and chemical reaction equilibrium in terms of dynamic molecular processes
- ◦ Apply the state postulate and the Gibbs phase rule to determine the number of required independent properties needed to constrain the state of a system (pure species)
- ◦ Identify the phases present on a PT and/or Pv diagram as well as the critical point and triple point
- ◦ Describe the difference between the saturation and vapor pressures
- Determine thermodynamic properties using both calculations and tabulated data [Ch 1.6-1.7]
- ◦ Read desired thermodynamic properties from steam tables
- ◦ Using linear, sometimes double, interpolation to calculate property values from sparse tabular data
- ◦ Use equations of state to calculate unknown properties from measured properties

---

TP: The origins of Thermodynamics

The origins of Thermodynamics

Thermodynamics began as a way to evaluate the potential of steam engines to provide work.
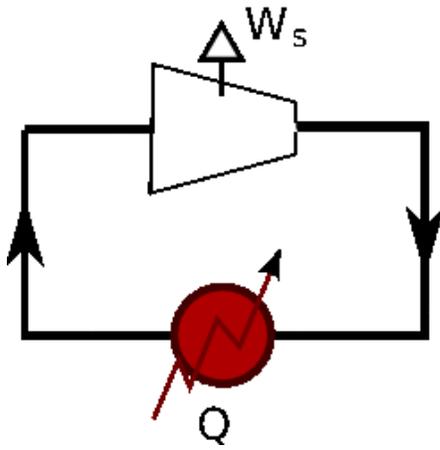
It is based on "laws" that are simple generalized statements that are consistent with all known observations.

NOTE:

It tells us nothing about rates. As we will see in the Transport Pillar, rates depend on driving forces and resistances. While Thermo tells us about driving forces, it tells us nothing about resistances.

NOTE:

Also, Thermo is a "macroscopic" science in that it cannot describe the molecular mechanisms of events (although a molecular viewpoint can help us understand Thermodynamic properties, as we will see).

TP: Thermodynamic Properties

Thermodynamic Properties

We will distinguish between the properties of a material in several different ways:

DEFINITION:

Measured properties *are properties that are directly accessible in the laboratory. Examples include: temperature, pressure, volume*

DEFINITION:

Fundamental properties *are properties that are directly related to the fundamental laws of thermodynamics. These are internal energy and entropy (both will be discussed later).*

DEFINITION:

Derived properties *are specific relations that include combinations of measured and derived properties. Examples include enthalpy, Gibbs free energy.*

NOTE:

Both fundamental and derived properties are ***unmeasurable***

Properties may be further classified in the following way:

DEFINITION:

*An **extensive variable** is one which depends on system size. Examples include mass, volume.*

While extensive variables are useful for characterizing the *specific* system being analyzed.

DEFINITION:

*An **intensive variable** is one which does not depend on system size. Examples include temperature, pressure, density.*

While it may not be immediately obvious, intensive variables tell us *more* about the system than extensive variables. In particular, the temperature and pressure are two of the most critical intensive variables.

NOTE:

*A **ratio** of extensive variables will yield an intensive variable! (For example, mass/volume -- two extensive variables -- gives density, an intensive variable) This is one way to understand why intensive variables "tell you more".*

OUTCOME

Distinguish between extensive and intensive thermodynamic properties

---

Scales of scrutiny

We will discuss three scales of scrutiny: Macroscopic, microscopic, and molecular.

Macroscopic refers to bulk systems that are readily observable.

Microscopic refers to regions that are smaller than those observable by the naked eye, but which contain sufficient numbers of molecules so that they may be considered "continuous".

The **molecular** scale refers to a region that is small enough that it includes individual atoms/molecules (so that thermodynamic properties are no longer continuous).

Measured Properties

- Amount: **Volume** $\to$ V [=] LxLxL extensive
  Mass/moles $\to$ M [=] M or N [=] moles extensive
  Intensive "volume" (often called **specific volume,**)

$\hat{v} = V/M$ or $v = V/N$

- **Temperature**: Always intensive. Refers to the degree of hotness. On a molecular scale it is a measure of the average kinetic energy of the molecules/atoms in a system (that is, E_k = (3/2) kT). Obviously, because it is an average, there will be a distribution of kinetic energies of the molecules. The distribution that is observed in gases is called the Maxwell-Boltzmann distribution and is how one determines when there are enough gas molecules in a sample to consider the continuum hypothesis (i.e., a macroscopic description of the material) to be valid.
- **Pressure**: Always intensive. Refers to the normal force per unit area exerted on a "surface". Pressure itself has no direction (it is a scalar quantity), but it can obtain a direction from the surface. The pressure in a continuous medium is the force exerted on a hypothetical surface. From a molecular viewpoint, this force is exerted due to the exchange of momentum between molecules and the surface during collisions with that surface (note that the units of force is the rate of change of momentum).

Converting between temperature scales:
- T(K) = T(C) + 273.15
- T(R) = T(F) + 459.67
- T(R) = 1.8*T(K)
- T(F) = 1.8*T(C) + 32

<div align="center">

NOTE:

</div>

*Converting temperature **differences** is slightly different (the additive corrections cancel out!).*

<div align="center">

TEST YOURSELF:

</div>

Convert 20C to F. How about R? Convert -40C to F :)

<div align="center">

TP: Work and Energy

Work and Energy

</div>

Recall that Thermo began as a way to evaluate the potential of steam engines. In other words, the goal was to ascertain how much work could be extracted from a given system.

<div align="center">

DEFINITION:

</div>

***Work** is the action of a force over a distance. In other words, moving stuff is doing work.*

$$dW = FdL = -PAd\left(\frac{AL}{A}\right) = -PdV$$

<div align="center">

NOTE:

</div>

The pressure has no direction thing is the origin of the - sign; specifically, since moving something requires *input* of work we need to calculate the work to compress something (which would cause a dV<0) in such a way as to give us a positive work.

Energy has the same units as work and can be thought of as somethings's ability to perform work (if you like).

DEFINITION:

Kinetic energy follows naturally from Newton's Law and can be thought of as energy related to motion:

$$dW = FdL = MadL = M(\tfrac{du}{dt})dL = M(\tfrac{dL}{dt})du = Mudu$$

integrating gives:

$$W = \tfrac{1}{2}M \, \Delta(u^2)$$

DEFINITION:

Potential energy can be thought of as energy related to position

$$dW = FdL = MgdL = Mgh$$

Defining problem regions

In attempting to apply the laws of Thermodynamics in such a way as to solve engineering problems, it is critical that we define exactly the region of space to which we are applying those rules.

DEFINITION:

*The **universe** is all of space.*

While the laws of thermodynamics could be applied to the universe, it is usually more convenient to break that space up into:
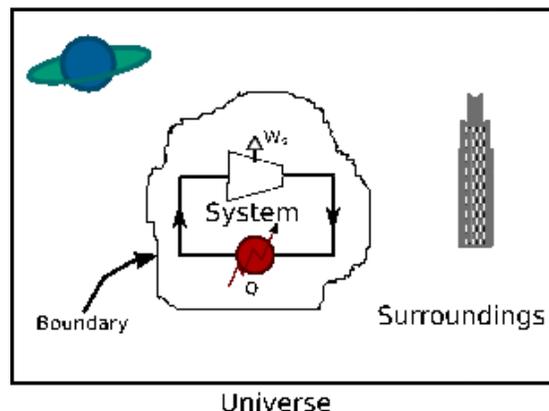
DEFINITION:

*The **system** is the region of space that is of interest in the problem.*

DEFINITION:

*The **surroundings** is all of the space which is not contained within the system.*

The system is enclosed by a boundary (that may be real or simply a "line"), so that the system can be open, closed, or isolated.

OUTCOME

Distinguish between the universe, system, surroundings, and boundary

---

Characterizing problem regions

Depending on the definition of our boundary, systems can be characterized in several ways.

DEFINITION:

*An **open system** is one where both mass and energy may cross the boundaries of the systems. Examples: pipes, turbines*

DEFINITION:

*A **closed system** is one where only energy may cross the boundaries (that is, mass cannot cross the boundary). Examples: an oven, this classroom*

DEFINITION:

*An **isolated system** is one which does not allow mass or energy to cross its boundaries.*

OUTCOME

Define open system, closed system, and isolated system

Thermodynamic States

DEFINITION:

*The **thermodynamic state** of a system is the condition in which it is currently in. Knowing the state fixes all of the system's intensive properties.*
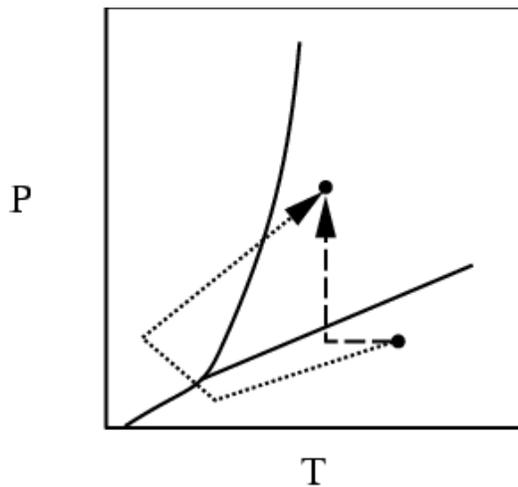
DEFINITION:

*A **process** is the act of bringing a system from one state to another.*

A process may be adiabatic, isothermal, isobaric, isochoric (also isenthalpic, isentropic, etc. but we will discuss those later).
- adiabatic = no heat exchange
- isothermal = constant T
- isobaric = constant P
- isochoric = constant volume

What is interesting about a process is that values of thermodynamic intensive properties do not depend on the path that the process takes from one state to the next. They simply depend on the states achieved.

DEFINITION:

*A **state function or property of state** is independent of path (only depends on state). Examples: T, P, v, u*

Because of this path independence, changes in the state functions are often calculated via paths that are simply convenient/hypothetical rather than real.

Nevertheless, there are other important quantities, such as heat and work, that are path dependent. These are often called path functions.

Explain the difference between state and path variables

TEST YOURSELF:

Is the specific volume of the following materials the same or different at the end of the process?

- 100.0 kg of methane gas initially at 100C is cooled to room temperature and atmospheric pressure
- 1.0 g of liquid methane at -10C is vaporized rapidly to form a gas at room temperature and pressure

While the answer to this question may not be immediately obvious, hopefully the answer to an analogous question is: what is the corresponding final height (above sea level) of each of the following students?

- Student A takes the bus from Shadyside, arrives at Benedum Hall and takes the elevator to the 12th floor
- Student B gets on a helicopter on Mt. Washington, lands on the room of Benedum Hall and climbs down the stairs to the 12th floor

---

TP: Thermodynamic Equilibrium

Thermodynamic Equilibrium

DEFINITION:

***Equilibrium** is the condition whereby there are no changes with time nor any tendency to change with time.*

Equilibrium implies:
- Mechanical equilibrium: $\sum F = 0$ or $P_{sys} = P_{surr}$.
- Thermal equilibrium: $T_{sys} = T_{surr}$.
- Chemical (and chemical reaction) equilibrium: no tendency to change phase or react (we will yield an equation to mathematically state this later).
- Phase equilibrium .....

OUTCOME:

Distinguish between equilibrium and steady state

TEST YOURSELF:

Explain why only closed systems may be in equilibrium.

TEST YOURSELF:

*Give examples of systems at steady state but **not** in equilibrium.*

TP: Phases and Phase Equilibrium

Phases and Phase Equilibrium
DEFINITION:

*A **phase** is a bit of matter characterized by uniform composition and physical structure.*

So in addition to the three "phases" of matter that we learn about in elementary school, here we will use phase in a different way. So we can have two coexisting liquid phases, two solid phases, etc.

NOTE

A phase need not be continuous. For example, an emulsion has two phases only one of which is continuous, while the other is "dispersed".

DEFINITION:

*When we have two coexisting phases, they are separated by a **phase boundary**.*

DEFINITION:

***Phase equilibrium** characterizes a system that has multiple coexisting phases whose individual phases (and their amounts) do not change and have no tendency to change on a macroscopic scale.*

Note that there will be microscopic transport across the phase boundary, but it will be balanced.

This means, for example, that the number of molecules that condense would be balanced by the number that vaporize.

OUTCOME:

Define the term phase and explain what it means for phases to be in equilibrium

---

TP: The State postulate and the Gibbs phase rule

The State Postulate and Gibbs Phase Rule

DEFINITION:

*The **state postulate** says that the thermodynamic state of a pure (singe-phase) substance may be uniquely defined by knowing two (independent) values of its intensive variables.*

TEST YOURSELF:

If you knew the temperature and pressure of an ideal gas could you calculate the specific volume?

DEFINITION:

*The **Gibbs phase rule** tells us that the intensive properties of a given phase may be uniquely identified by knowing D (independent) intensive variables where D is given by*

$$D = c - \pi + 2$$

c = # of components

π = # of phases

NOTE:

The T and P in a multiphase mixture would count toward both phases!

However, in order to constrain the state of the system we need to know independent intensive variables, so we need to be careful with this information.

DEFINITION:

*The **quality** of a vapor-liquid mixture is the mole fraction of the mixture that is vapor.*

TEST YOURSELF:

How many intensive variables do you need to know to determine the state of melting ice? How about a mixture of melting ice and some of the (already melted water)?


TP: Phase Diagrams

Phase diagrams

A pure substance cannot occupy any arbitrary point on the P,T, v space, instead being confined to a surface (i.e., any two that are identified specify the third).

For this reason, one often visualizes the phase behavior of a species by taking a projection of the PvT spaces in two dimensiones: typically in the P-v or P-T plan.

DEFINITION

*A **PT diagram** shows the phase behavior of a single species in the pressure-temperature plane. Here, lines denote the boundaries between phases (or the points where the phases coexist).*
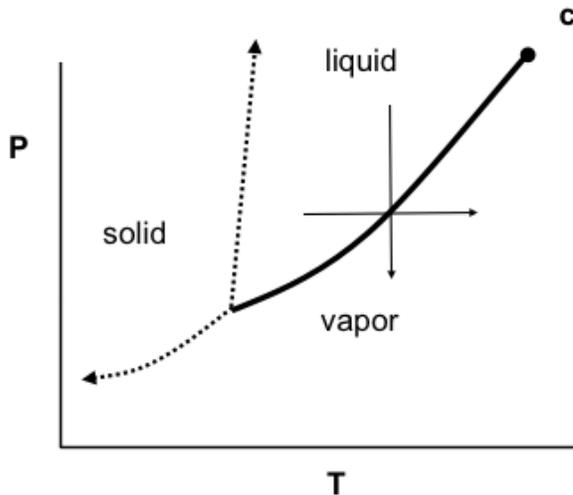
- L to V by increasing T or decreasing P
- Transition : **boiling point** or **condensation point**
- Boiling points line on a **coexistence curve**
- Coexistence extends from **triple point** to **critical point**
- Appendix B1, B2

DEFINITION

*The **saturation pressure** is the coexistence pressure between liquid and vapor for a pure species and is a function of temperature (only). (see state postulate)*

NOTE

*While the **vapor pressure** is similar to the saturation pressure, the vapor pressure refers to the pressure in a mixture of components (i.e., the total pressure is higher).*

OUTCOME:

Describe the difference between the saturation and vapor pressures
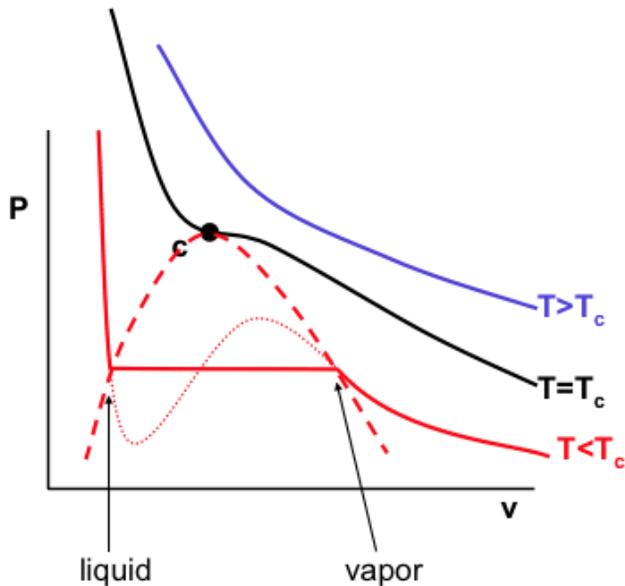
Coexistence on a Pv diagram is shown on the liquid-vapor dome, since v is very different for liquids and vapors (up to the critical point!).

NOTE

*A **supercritical fluid** is a substance which is above its critical temperature, Tc. Here there is no vapor-liquid transition so the liquid-vapor dome ends.*

DEFINITION:

- **Saturated** essentially means "in phase equilibrium"
- **Superheated** means at a temperature above the saturation/coexistence curve
- **Subcooled** means at a temperature below the saturation/coexistence curve
- Appendix B1, B2

On the vapor-liquid line the temperature is called the **boiling point** and the pressure is the **vapor pressure**.

On the vapor-solid line the temperature is called the **sublimation point**.

On the liquid-solid line the temperature is called the **freezing/melting point**.

OUTCOME:

Identify the phases present on a PT and/or Pv diagram as well as the critical point and triple point

---

TP: Using "Steam" Tables (and other tabulated data)

Using "Steam" Tables (and other tabulated data)

Recall that the state postulate tells us that knowing two intensive variables of a pure species fixes all others (i.e., the state).

DEFINITION

*A **"steam" tables** typically organize u, s, h, v, and sometimes g state functions according to (typically) T and P.*

In our book, the steam tables (See Appendix B) include:
- 2 tables for vapor-liquid
- 1 for vapor-solid
- 1 for superheated vapor
- 1 for subcooled liquid.

OUTCOME:

Read desired thermodynamic properties from steam tables

NOTE

Often the quantity of interest does not fall at exactly the tabulated properties.

DEFINITION:

Interpolation *is the calculation procedure that assumes a straight line between neighboring "points" in a table or figure in order to estimate an intermediate value.*

$$\frac{y-y_1}{y_2-y_1} = \frac{x-x_1}{x_2-x_1}$$

$$y = y_1 + (y_2 - y_1) * \left(\frac{x-x_1}{x_2-x_1}\right)$$

NOTE:

If both known properties are intermediate to the tabulated data, ***double*** *interpolation is necessary.*

OUTCOME:

Using linear, sometimes double, interpolation to calculate property values from sparse tabular data

TEST YOURSELF:

Calculate the specific volume of superheated water vapor (see Appendix B.4) at 230 kPa and 460 ∘C.

TP: Ideal Gas Law and Equations of State

Ideal Gas Law
DEFINITION

An ***equation of state*** *relates the molar density (or specific molar volume) of a fluid (i.e., a vapor or a liquid) to the temperature and pressure of the fluid.*

The most common and simplest equation of state is the ideal gas law:

$$P = \frac{nRT}{V} = \frac{RT}{v}$$

NOTE

Interestingly, the ideal gas law can be derived from our molecular understanding of the properties T and P. This requires that we

assume that gas molecules are infinitely small and interact only via collisions.

IMPORTANT

The ideal gas law is an approximation (!) that has only limited applicability. It is usually used for diatomic gas when (RT/P)>5 L/mol and for other gases when (RT/P) > 20 L/mol (i.e., at high specific volumes!).

OUTCOME:

Use equations of state to calculate unknown properties from measured properties