## Lecture 10

# Heat Capacities and Gaseous Behavior

<u>Last Time</u>

**PV Work for Fluids**

**Cycles as Demonstration that Work is not a State Function**

**A Cycle as a Limiting Case of a Quasi-equilibrium Process**

**Maximum Work and Reversible Processes**

**Heat Capacities**

## Gaseous Capacities at Constant Volume or Pressure

$C_V$ is the heat capacity for an ideal fluid substance for processes in which *no work is done.* There would be equivalent "no-work" heat capacity in more complex materials.

$C_P$ is the heat capacity for an ideal fluid substance for processes in which *an intensive variable is held fixed.*

Consider identical ideal fluid systems, that receive the exact same amount of heat by a constant volume (isochoric) process and by a constant pressure (isobaric) process:

$$q = \int_{T_\circ}^{T_V} C_V dT = \int_{T_\circ}^{T_P} C_P dT \tag{10-1}$$

We can make a hand-waving argument that the temperature, $T_P$, reached during the constant pressure process is smaller than $T_V$.

No work is done for the constant volume process, so $\Delta U_V = q$. Let's imagine that a new process is added to the end of the constant volume process that takes it to the same state as the end of the constant pressure process (i.e, let it expand by reducing the applied pressure). It is clear that we can extract work from this added process because the fluid can do work on its surroundings as it expands—therefore it should be possible to store this work and then pass it back to the system as heat at constant volume, thus increasing the temperature. Since the final state is the same, it follows that $T_P < T_V$, therefore, using the intermediate value theorem of basic calculus:

$$\begin{aligned} (T_V - T_\circ)\langle C_V \rangle &= (T_P - T_\circ)\langle C_P \rangle \\ \frac{C_P}{C_V} &= \frac{T_V - T_\circ}{T_P - T_\circ} > 1 \end{aligned} \tag{10-2}$$

For larger thermal expansion, the difference in heat capacities will be greater.

Gases, which expand considerably with temperature, have a large difference in their heat capacities.

Liquids do not expand as much. For $H_2O$ at 15°C and $P = 1$ atm, $c_P = 1\text{cal}/(°\text{Kgram})$. (Note use of little $c$ for the derived intensive quantity on a per mass basis), and $c_V$ is only slightly different.

For solids, the difference is very small and usually neglected.

## Models for Gaseous Behavior

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Experimental Observations:

**Boyle's Law**: At constant temperature. The pressure of a fixed amount of a gas varies inversely with its volume.

$$P = \frac{\text{constant}}{V} \quad \text{or} \quad PV = \text{constant} \tag{10-3}$$

*Question: How would you show this experimentally?*

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**Charle's Law (or Gay-Lussac)**

The constant from Boyle's Law varies approximately linearly with the temperature of the gas.

$$PV = \text{constant}_2 T \tag{10-4}$$

from which follows (since $V$ is extensive):

$$PV = nRT \tag{10-5}$$

Traditionally, $R$ is used when $n$ is the number of moles, but we could define it as the molar version of Boltzmann's constant: $\overline{k} = R$.

For a general, (nonpolar, non-magnetic, non-anything-else-that-can-store-work) fluid, we can write a state function

$$T = f(N, P, V) \tag{10-6}$$

The ideal gas is just one example of such a function:

$$PV = nRT \quad \text{or} \quad P\overline{V} = RT \tag{10-7}$$

$$dT = \frac{\partial T}{\partial P}dP + \frac{\partial T}{\partial V}dV + \frac{\partial T}{\partial N^{\text{total}}}dN^{\text{total}}$$

$$= \frac{V}{Nk}dP + \frac{P}{Nk}dV - \frac{PV}{N^{\text{total}^2}k}dN^{\text{total}}$$

$$= \frac{T}{P}dP + \frac{T}{V}dV - \frac{T}{N^{\text{total}}}dN^{\text{total}}$$

(10-8)

$$d\log T = d\log P + d\log V - d\log N^{\text{total}}$$

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An ideal gas can be thought of a set of point particles that have no finite range forces interactions–this is clearly an idealization, since we know that molecules take up a finite amount of space and that forces can exist between gas molecules.

On closer examination of experimental data, it is found that gasses only approximate this behavior; van der Waals added a few extra constants to fit the data better:

$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$$

(10-9)

When $a = b = 0$, Equation 10-9 is the same as Equation 10-5.

$b$ accounts the finite size of the molecule.

$a$ is a measure of forces between molecules thus affecting pressure.

Both Equation 10-9 and Equation 10-5 are models for material behavior. They are independent of thermodynamic principles, but the behavior of any material is subject to the laws of thermodynamics. So, thermodynamics limits the types of equations that can be used as state functions for material behavior.

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