

## Chapter 5: Heat Capacity and Conductivity of Gases

### *Thermal Energy Exchange defined by Heat Capacity*

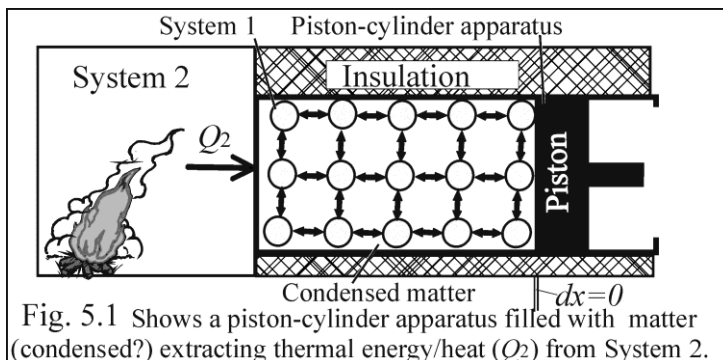
Remember, thermal energy is herein considered as being the energy/radiation that when absorbed, results in intermolecular, and/or intramolecular vibrations within condensed matter.

Assume that Systems 1, and 2, are in physical contact with each other, and that thermal energy from System 1 ( $Q_1$ ), enters System 2. Then the change to the thermal energy ( $dE_{T1}$ ) within System 1, in differential format would be:

$$dE_{T1} = Q_1 \quad 5.1$$

$dE_{T1}$  can be calculated in terms of the heat capacity ( $C_{y1}$ ), and how much the temperature change of System 1. The heat capacity ( $C_y$ ) is generally expressed on either per mole or per unit mass basis, with the subscript "y" signifying the parameter ( $P, V$ ) that is considered as being constant.

Dealing with condensed matter is straightforward. Fig. 5.1 shows System 1 consisting of condensed matter within a piston-cylinder, which is being heated by System 2. Consider a total thermal energy ( $Q_2$ ) flows from System 2 into System 1 causing an isometric ( $dx \approx 0$ ) temperature increase ( $T_1 \uparrow$ ) within System 1, i.e. an increase in System 1's molecule's vibrational energies (both intermolecular and intramolecular).



Based upon then eqn 1.28:  $C_v = (1/m)(dQ/dT)_v$  then in terms of the mass ( $m_1$ ) within the piston-cylinder apparatus, the change in energy is:

$$dE_{T1} = dQ_1 = m_1 C_{v1} dT_1 \quad 5.2$$

If system 2 was a closed system ( $m_2$ ) rather than a continual heat source i.e. fire, then in terms of the heat capacity ( $C_{y2}$ ) of System 2, and the exchange of thermal energy:

$$dE_{T2} = -dQ_2 = m_2 C_{v2} dT_2 \quad 5.3$$

Conservation of energy dictates that in terms of flowing thermal energy:

$$dQ_1 = -dQ_2 \quad 5.4$$

And in terms of total net thermal energy that has flowed between the two systems:

$$Q_1 = -Q_2 \quad 5.5$$

The above was based upon the system's mass. Note: Engineers prefer to use heat capacity per unit mass<sup>1</sup>, while chemists/scientists prefer per mole<sup>2,3</sup>, and physicists often use per molecule.

### *Total Energy within a System*

Could the total thermal energy contained within any system be approximated by using eqn 5.2, and considering that the temperature change starts at absolute zero ( $-273.15 \text{ }^\circ\text{C} = 0 \text{ K}$ ), and goes to the final

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temperature ( $T_{if}$ ) in question, e.g. room temperature (293 K). This assumes that the heat capacity is constant throughout all temperature regimes. It must be understood that this is not necessarily the case. As was pointed out by Planck<sup>4</sup> heat capacities can be approximated as constant through temperatures between 0°C and 100°C. However it cannot be assumed to be the case for all temperatures. Actually our expectation should be as a system approaches absolute zero then the notion of constant heat capacity needs reconsideration. Ditto for high temperature i.e. blast furnaces temperatures. This will make more sense after the Sun's input is discussed in Chapter 8.

Accordingly, obtaining the isometric heat capacity from tables, and knowing a substance's temperature, allows us to only roughly approximate how much thermal energy is contained in a given system. Hence, in terms of the isometric molar heat capacity ( $C_{v1}$ ) and the final absolute temperature ( $T_{f1}$ ), as a rather loose approximation, the total thermal energy ( $E_{T1}$ ) in some system 1, consisting of  $n$  moles can be written as:

$$E_{T1} \approx nC_{v1}T_{f1} \quad 5.6$$

### Gases: Total Energy & Gas Constant

In Chapter 2, the total kinetic energy ( $E_{Tk}$ ) of a system of  $N$  gas molecules was defined by eqn 2.12:  $E_{Tk(t,r)} = 3NkT/2$ . For a volume of monatomic gas with a sufficient number of molecules, and at a moderate temperature, then the total energy of that gas can be approximated as being purely kinetic (rotational plus translational). For such a monatomic gas, eqn 5.6 should equate to eqn 2.12:

$$E_T \approx nC_vT = 3NkT/2 = 3nRT/2 \quad 5.7$$

Based upon eqn 5.7, obviously:

$$C_v = 3R/2 \quad 5.8$$

Now reconsider a rough approximation for the energy of any gas, as defined by eqn 2.19:  $E_T \approx NkT(n''+1/2)$ . Therefore, for " $n$ " moles of gas molecules, the rough approximation becomes:

$$E_T = nRT(n''+1/2) \quad 5.9$$

Remember herein  $n$  represents the number of moles (a mole contains  $6.02 \times 10^{23}$  molecules) while  $n''$  represents the number of atoms within each gas molecule.

### Heat Capacity of Gases

The heat capacity of a gas is often empirically obtained by heating a wire surrounded by the gas in question, which is then surrounded by a coaxial cylinder, as illustrated in Fig 5.2. Reconsider eqn 5.9. Dividing through by temperature, the total thermal energy for a mole of gas molecules per degree temperature is:

$$E_T/T = R(n''+1/2) \quad 5.10$$

The total energy per degree temperature is the heat capacity. For the temperature regimes that are generally experienced here on Earth, the heat capacity is constant. Now eqn 5.10 can be rewritten in terms of the molar isometric heat capacity ( $C_v$ ), i.e.<sup>5</sup>:

$$C_v = R(n''+1/2) \quad 5.11$$

The difference between isobaric heat capacity ( $C_p$ ) and isometric heat capacity ( $C_v$ ) for a mole of ideal gas molecules is the ideal gas constant ( $R$ ) i.e. eqn 1.32:  $R = C_p - C_v$ . Based upon

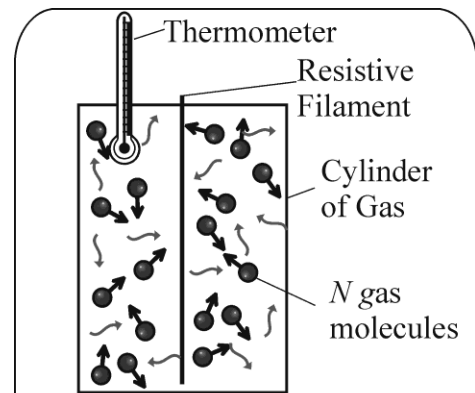


Fig. 5.2 Shows a hypothetical system for measuring a gas's specific heat. A gas in a cylinder, at pressure:  $P_g$  and temperature:  $T_g$ , is surrounded by walls at temperature:  $T$ . In thermal equilibrium:  $T=T_g$ . The gas is heated by electricity in the resistive wire and its temperature change is measured by the thermometer.

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equations 1.32 & 5.11, the general equation for a gas's isobaric heat capacity becomes<sup>5</sup>:

$$C_p = R(n''+1/2) + R = R(n''+3/2) \quad 5.12$$

In Chapter 1, it was discussed that the adiabatic index ( $\gamma$ ) is the ratio of heat capacities, which is given by:  $\gamma = C_p / C_v$ . Dividing eqn 5.12, by eqn 5.11, gives<sup>5</sup>:

$$\gamma = C_p / C_v = (n''+3/2)/(n''+1/2) \quad 5.13$$

Based upon the above equations, the following Table 5.1 is obtained, which is in very good agreement with the empirically proven values for the heat capacities of gases<sup>1</sup> for small  $n''$ . The empirically determined adiabatic indexes ( $\gamma$ ) are shown in Table 5.2.<sup>5</sup>

Table 5.1

Type of gas	$n''$	$C_v$	$C_p$	$\gamma$
Monatomic	1	$3R/2$	$5R/2$	1.66
Diatomic	2	$5R/2$	$7RT/2$	1.40
Triatomic	3	$7RT/2$	$9RT/2$	1.29

Table 5.2

Monatomic	$n''=1: \gamma$	Diatomic	$n''=2: \gamma$	Triatomic	$n''=3: \gamma$
He	1.667	H <sub>2</sub>	1.405	CO <sub>2</sub>	1.289
Ne	1.667	N <sub>2</sub>	1.4	NO <sub>2</sub>	1.27
Ar	1.667	O <sub>2</sub>	1.395	H <sub>2</sub> S	1.32
Kr	1.665	OH	1.384	SO <sub>2</sub>	1.29
Xe	1.65	CO	1.40		

### ***Traditional Analysis and Heat capacity Discussion***

As was discussed in Chapter 2; the analysis given herein for heat capacities of gases does differ from the traditional degrees of freedom based analysis<sup>5</sup>. Since this author does not embrace the degree of freedom argument, it is left to the reader to decide: Occam's razor? Importantly, our analysis better explains empirical data. The fact that our interpretation of heat capacity fits so well with theory for triatomic, diatomic and monatomic gases should make traditionalists at least ponder. Note the traditionally accepted value equals our theoretical values for both monoatomic and diatomic. However for triatomic the traditionally accepted value is 24.9 [J/(mol\*K)].

Even for  $n''=4$ . The fit is perfect for many gases like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>:  $C_v = 37.8$ ,  $C_p = 46.1$ ) & acetylene (C<sub>2</sub>H<sub>2</sub>:  $C_v = 35.7$ ,  $C_p = 44.0$ ) the fit is rather good with our theoretical values ( $C_v = 37.4$ ,  $C_p = 45.7$ ). However, consider ammonia (NH<sub>3</sub>:  $C_v = 27.34$ ,  $C_p = 35.7$ ) which is not a very good fit. Is there a difference between these molecules? On a rudimentary level both hydrogen peroxide and acetylene are bent elongated molecules while ammonia is pyramidal. The implication maybe molecular shape or size affects how it interacts with either the walls or surrounding blackbody/thermal radiation.

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### A Larger Data Set

It is hard to make conclusions based upon such a small data set. Table 5.4 provides a more encompassing data set for the accepted isometric and isobaric molar heat capacities for various substances for;  $0 > n'' > 27$ . These accepted values were calculated using an engineering table from Rolle's book<sup>1</sup> as is shown in Table 5.5. Note engineer's specific heats are on a per mass basis, while scientists prefer heat capacities that are on a per mole basis. Table 5.4 and Table 5.5 are located at the end of this Chapter.

In Graph 5.1, both the isometric and isobaric theoretical (based upon equations 5.11 and 5.12) molar heat capacities are sketched against the number of atoms/elements ( $n''$ ) in each molecule<sup>5</sup>. The accepted values for heat capacities vs number of atoms/elements are taken from Table 5.4 and are roughly plotted. As previously stated, our theory and accepted results are a very good fit up for  $n'' < 4$ . What was not expected is the fact that the slope of the accepted values graph is visually very close to the slope of accepted value for  $n'' > 9$ . This can only be explained in terms of vibrational energy, as is done herein.

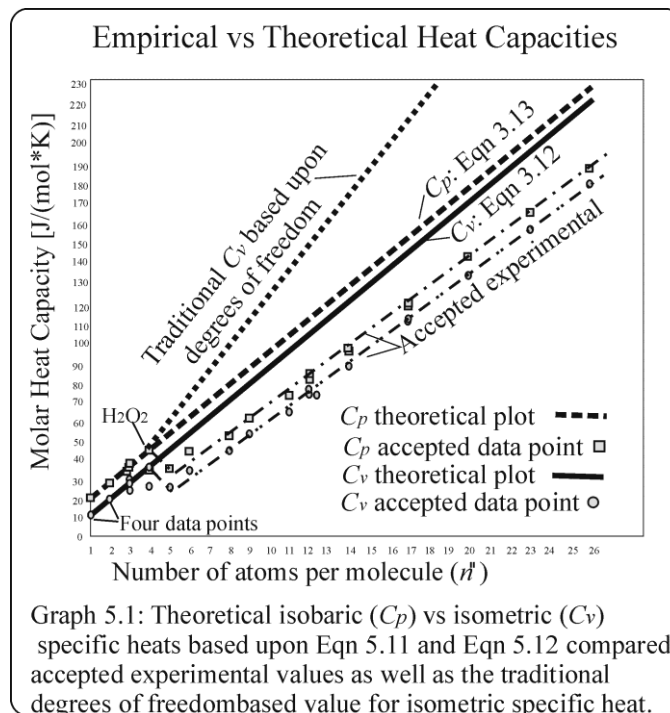
When compared to the traditional accepted theoretical curve it is obvious that the theory presented herein (Chapter 2 and herein) verges on inarguable. Remember the traditionally accepted theory is based purely upon mathematics (degrees of freedom) rather than being enshrined in inherent logic.

#### Possible Reason for Discrepancies

Why the discrepancy exists for  $n'' > 4$  may be open for debate! Certainly preliminary questions arise, such as: Does the shape affect how a gas molecule absorbs surrounding thermal radiation? Or: Does the shape influence the exchange of various energies (translational & rotational plus vibrational) with wall molecules? Perhaps elongated linear molecules and/or large molecules tend to "flatline" against the wall as is illustrated in Fig 5.3 at location A. The implication being that large and/or elongated gas molecules tend to hit several (few or more) wall molecules at once, with some vibrating wall molecules moving inwards, while others are moving outwards, thus affecting the cleanliness of kinematic energy exchanges.

To better understand consider the small monatomic gas molecule hitting location C. Here the wall molecule is moving outward from the wall thus instantly imparting momentum, hence pumping kinetic energy onto the gas molecule during collision. Next consider the gas molecule hitting at location B. Although the wall molecule and gas molecule are initially moving in the same direction, i.e. both into the wall, since the wall molecule is vibrating at such a high frequency then within a fraction of a nanosecond the wall molecule will start moving in the opposite direction. At which point the wall molecule imparts momentum hence kinetic energy (translational plus rotational) onto the now colliding gas molecule.

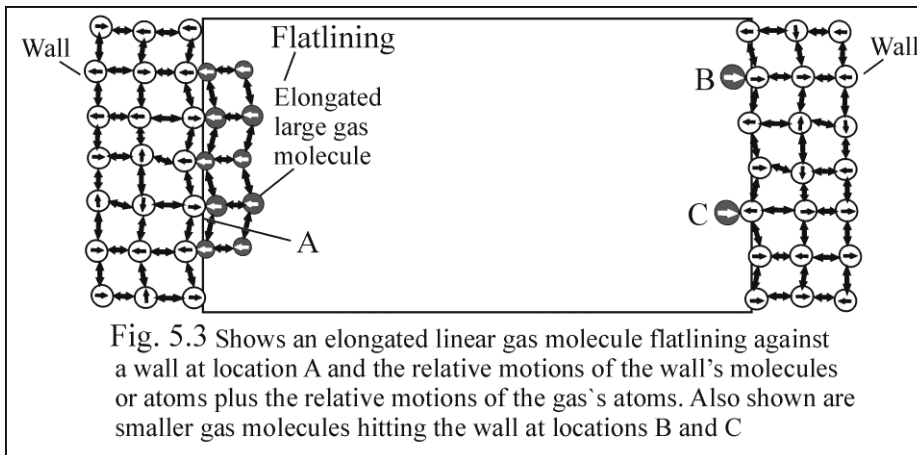
Accordingly, small gas molecules ( $n'' < 4$ ) should have the ability of interacting with a wall molecule



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cleanly, which is to say that the significantly larger vibrating wall molecule pumps its mean kinetic energy directly onto the small gas molecule. Seemingly, this is not the case for larger molecules, where kinetic (translational plus rotational) energies tends not be cleanly/clearly transferred.



Furthermore, although our theoretical analysis does parallel the accepted experimental findings reasonably well for  $n \gg 4$ , as shown in Graph 5.1, the slope of accepted data is slightly less than our analysis predicts. This author further wonders if collisions between larger vibrating gas molecules with vibrating wall molecules can be considered as *completely inelastic*. By completely inelastic it is meant that a significant amount of heat/thermal energy is given off during such a collision but the net exchange of kinetic energies is indeterminable. This too would alter one's experimental expectations and may be best explained in terms of what is discussed.

Reconsider Joules weight experiment as was discussed in Chapter 1. Does the fact that the increased motions in the liquid mean that intermolecular friction has increased, hence even in the liquid state intermolecular collisions are inelastic? Seemingly, yes!

Another plausible explanation is that differing polyatomic gaseous configurations possess different vibrational energies at a given  $T$ ? Of course this all may require extensive thought and/or modeling!

### *New Discussion*

In the preface of this book it was stated that the first step to solving any problem is asking the right question. Seemingly one of the first questions that should have been asked concerning thermodynamics being; what is the fundamental difference between energy and work?

### *Work versus Energy*

In Chapter 4 the essentials of work was discussed. Let us highlight some of what was discussed. Although work and energy can both be defined in terms of so many Joules of energy, one could say that energy has no sense of direction while work is performed with a unique direction in mind. Or that energy of a gas exists along all axes equally in all directions, while work is performed along a solitary axis and is powered by energy impacting a plane perpendicular to that axis. Of course there is more to it than this.

On Earth work moves machines and/or man in a particular direction whether it be up, down, right or left. When work is performed and directed upwards, it generally involves the movement of a mass against gravity, resulting in a potential energy increase onto that mass.

And when a system expands, it does not matter in which direction the expansion is, the net result is the upward displacement of our atmosphere ( $W_{lost} = P_{atm}dV$ ), or at least the equivalent; whether that is a regional pressure increase or the heating of the atmosphere (direct or indirect). Certainly the atmosphere cannot be displaced in any direction other than upward, because downward would require the

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compression of the Earth itself while sideway would require the compression of the atmosphere, which is feasible but that is a regional pressure increase.

Even if you considered the formation of our solar system or any other galactic entity, this involves energy with a sense of direction, which involved work! Again the sense of direction that gravity provides differentiates work from pure stored energy.

Furthermore in our new perspective, the ability of a gaseous system to perform work, as a function of its temperature, is defined by the ideal gas law i.e.  $PV = NkT$ . While, the energy associated with a monatomic gas is defined by eqn 2.12:  $E_{Tk(t,r)} = 3NkT/2$ . Comparing, seemingly an ideal monatomic gas's ability to do work represents only 2/3 of that gas's kinetic energy at a given temperature. Ditto for change, i.e. eqn 4.19:  $d(E_{Tk}) = (3/2)NkdT$  vs eqn 4.20:  $W = d(PV) = NkdT$ . Seemingly the sense of direction that work has puts a 66.67% upper limit to the efficiency because all of the system's gaseous molecules cannot contribute all of their momentum to performing work.

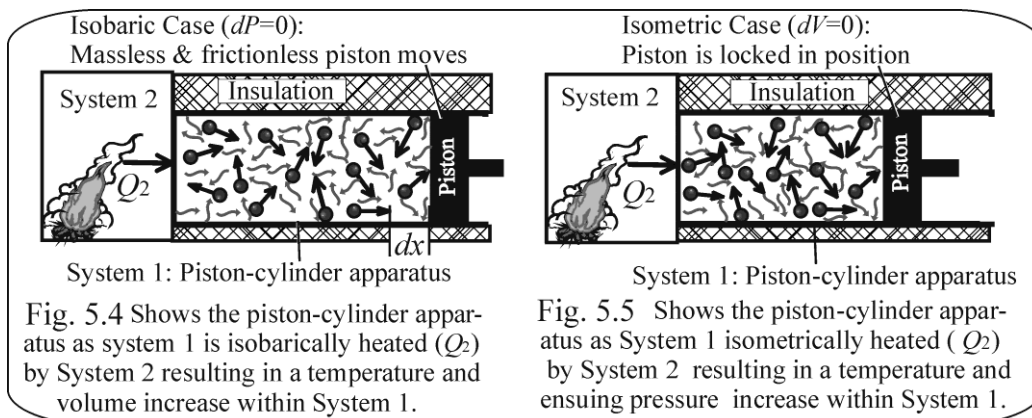
Another way of viewing this; when a monatomic gas is heated, all the molecules within a closed system will experience an increase in kinetic (translational plus rotational) from all directions (+/- x, +/- y, +/- z). Only 2/3 of the gas's kinetic energy increase can impart all of the increased momentum can be used for work to be done.

### What about Vibrational energy?

It makes for interesting conjecture to ask; to what extent can the vibrational energy of polyatomic molecule contribute to work? Assuming that the vibrational energy of diatomic, triatomic and other polyatomic molecules is strictly/primarily due to the absorption and radiation of surrounding blackbody/thermal radiation, the answer seemingly is that vibrational energy does not contribute to work.

Of course the above assumes that all parts of the system is always exactly in thermal equilibrium. It also assumes that polyatomic molecules receive as much vibrational energy from, as is gives onto, all walls during all energy exchanges/impacts. Such assumption may not be true at all times in all situations.

### Proof



What is the proof for all of our reconceptualization of lost work? Part of the proof lay in the differences between isobaric and isometric specific heat of gases, which was briefly discussed in Chapter 4. Investigating further; consider Figs 5.3 and 5.4. Both show System 2 giving the same amount of heat ( $Q_2$ ) into System 1, that being a piston-cylinder apparatus. For the isobaric case in Fig. 5.4, the heating of the gas causes a kinetic energy increase of the gas, which then drives the piston outwards by a distance,  $dx$ . Considering that the piston is both frictionless, and massless, then all the work that is actually done by the heating is done onto the atmosphere's displacement;  $W = P_{atm}dV$ . Herein;  $T_{system1} > T_{surroundings}$ .

Conversely, for the isometric case (Fig. 5.5), the piston is locked in place. Thus the heating of the gas

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results in a kinetic energy increase of the gas, which increases the pressure within the apparatus. Since no work is actually done, then the amount of heat required to raise the temperature of the gas inside the piston-cylinder must be less than it would be for the isobaric case. Again;  $T_{system1} > T_{surrounding}$ .

If the input of energy is the same for both the isometric and isobaric cases, then the temperature increase in the isometric case will be greater than in the isobaric case. This is because for the isobaric case work is done ( $W = P_{atm}dV$ ) onto the surrounding atmosphere.

Of course, if the piston in the isometric case is unlocked then work will be done onto the atmosphere, and either: 1) the gas will cool if the heat ( $dQ_2$ ) is turned off. Or: 2) Extra heat will be required in order for the gas to remain isothermal. We now begin to understand the differences between isometric and isobaric heat capacities for gases.

The heating process can be described in terms of the isometric heat capacity, i.e. eqn 1.31:  $C_v = (1/n)(dQ/dT)_v$ . Consider  $Q_1$  to be the total thermal energy input for  $n$  moles of gas becomes:

$$Q_1 = nC_v dT \quad 5.14$$

For  $n$  moles of monatomic ideal gas, in terms of gas constant ( $R$ ),  $C_v = 3nR/2$  hence

$$Q_1 = 3nRdT/2 \quad 5.15$$

Equally, this process can be rewritten in terms of  $N$  molecules and Boltzmann's constant ( $k$ ).

$$Q_1 = (3/2)Nk(T_{1f} - T_{1i}) \quad 5.16$$

Next reconsider the isobaric heating as shown in Fig 5.4. The piston is not locked thus the system readily expands. If the piston is both massless and frictionless then in order for the piston to move  $P_1$  only need be infinitesimally greater than 1 atm. In order for the piston to keep moving right, the temperature of the gas must be constantly increasing. The heating of the gas can be described in terms of the isobaric heat capacity, i.e. eqn 1.30:  $C_p = (1/n)(dQ/dT)_p$ . For  $n$  moles of gas:

$$Q_1 = nC_p dT \quad 5.17$$

Herein, not only is the gas heated but work is also done onto the Earth's atmosphere, where the energy involved is quantified by eqn 3.28:  $W_{done} = d(PV)_{atm} = P_{atm}dV$ . Accordingly, the heat in ( $Q_1$ ) in terms of isometric heat capacity plus work done onto the atmosphere is:

$$Q_1 = nC_v dT + P_{atm}dV \quad 5.18$$

Rewriting in terms of  $N$  molecules and Boltzmann's constant ( $k$ ).

$$Q_1 = (3/2)Nk(T_{1f} - T_{1i}) + P_{atm}(V_{1f} - V_{1i}) \quad 5.19$$

Since the ideal gas law applies then eqn 4.26 can be rewritten as:

$$Q_1 = (3/2)(P_{1f}V_{1f} - P_{atm}V_{1i}) + P_{atm}(V_{1f} - V_{1i}) \quad 5.20$$

In eqn 5.20:  $P_1 > P_{atm}$ . If the piston no longer moves, then:  $P_1 \approx P_{atm}$  and eqn 5.20 for the system of monatomic gas becomes:

$$Q_1 \approx (5/2)P_{atm}(V_f - V_i) \quad 5.21$$

Remember: In the above analysis the gas molecules were considered to be ideal and monatomic. For polyatomic molecules, one would need to also need to consider any changes to the gas's vibrational energy. See: Chapter 5 or to use either eqn 5.17 or 5.18 and apply the correct heat capacity for that gas.

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### Adiabatic index

It was previously seen that the adiabatic index, when comparing empirical values to our eqn 5.13  $\gamma = C_p/C_v = (n''+3/2)/(n''+1/2)$  fit well for  $n'' < 4$ . Looking at Graph 5.2 we can see that the spread of values for the adiabatic index ( $\gamma$ ) seems to increase for  $4 < n'' < 9$ . Interestingly, for larger  $n'' > 12$  our eqn 5.13 predicted values approximates the accepted values.

An interesting aspect of this is that this helps to affirm that the ideal gas constant ( $R$ ) is independent of the type of gas. Seemingly this confirms that our explanation of work being done onto the surrounding atmosphere simply makes sense over any illogical association with the entropy increase within an expanding system of gas.

### Other Temperature Regimes: Approaching Absolute Zero

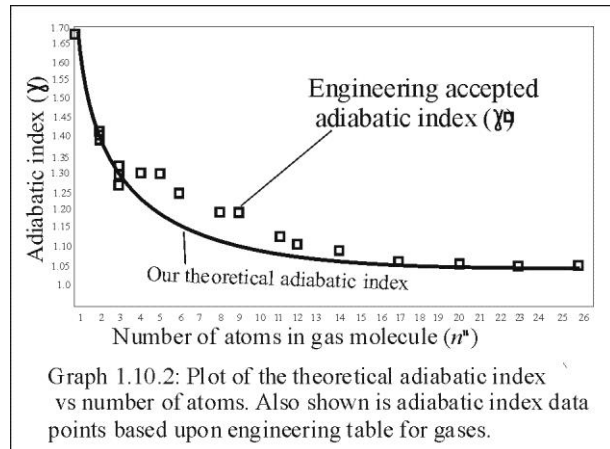
It is also accepted that the heat capacity of gases is not constant through all temperature regimes. The traditional explanation for low temperature change to the heat capacity is that the rotational energy is frozen out as systems approach absolute zero. This author would be more comfortable with thinking that the vibrational energies are frozen out at low temperatures. It seemingly makes more sense to say that at cold temperatures there is little to no vibrational energy within a gaseous molecule, as well as condensed matter. Since both the translational & rotational energy are pumped into the gas from the wall's vibrational energy, then as this vibrational energy declines, then so to do the gas's kinematic energy. Where is the logic in thinking that any of this does not also occur at exceptionally low temperatures, as some seemingly like to profess?

There may be more to it than this. Assume that there are no unaccounted for seepages of energy into or out of the experimental apparatus. Now consider that as  $T \rightarrow 0$  the thermal energy density within any substance is no longer directly proportional to its temperature. This is to say that the energy related to a molecule's translation, rotation, and vibrational, as well as any surrounding thermal/blackbody radiation is no longer linearly proportional to temperature.

In order to begin your understanding, just consider low temperature blackbody radiation i.e. blackbody radiation at 3 K, wherein the energy density curve peaks at  $\lambda \approx 1$  mm. Obviously, the thermal energy (i.e. infrared) would no longer be proportional to  $T$ , as it is for our Sun's radiation normally witnessed here on Earth. This is not to say that absolute zero does not represent the point that all matter is completely frozen. It is just to acknowledge that thermodynamic relations are no longer linear function of temperature, when near absolute zero. The exactness of this statement may vary depending upon the substance in question and in what manner it is viewed. This will be discussed in more detail in Chapter 8.

Even compare blackbody radiation of 3 K to 300 K, where the peak of the radiation curve occurs in the infrared,  $\lambda \approx 10 \mu m$ . Obviously, there must be a point between 3 K and 300 K wherein there is simply not enough thermal energy (i.e. infrared frequencies) to cause any real significant measurable molecular vibrations. Based upon published heat capacity curves, this seemingly happens when temperature drop below 100 K.

It must be emphasized that up to this point the thermal energy density within matter has unwittingly been considered to be linearly proportional to temperature, which is not the case for all  $T$ !



Graph 1.10.2: Plot of the theoretical adiabatic index vs number of atoms. Also shown is adiabatic index data points based upon engineering table for gases.



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### ***Thermal Conductivity & Gas***

The thermal conductivity of a gas is a cause for an interesting discussion. Back in Chapter 1, the thermal conductivity was defined by eqn 1.36:  $dQ/dt = -\kappa dT/dZ$ . It was discussed that there resides thermal radiation within a vacuum. Accordingly, if in a vacuum one wall were at a higher temperature than another wall directly across from it, then net heat would be transferred from the hot to the cold wall, through the emission and absorption of thermal photons, within the blackbody radiation spectrum. This would continue until thermal equilibrium between the two walls, was attained.

Instead of a vacuum, consider that the vessel contains a gas where the gas molecules dramatically increase the rate at which thermal energy is exchanged between the two walls, thus decreasing the time required for thermal equilibrium to be attained. Moreover, the rate of thermal energy exchange is not universal for all gases, i.e. it is gas dependent.

Theoretically, the kinetic energy of all monatomic gases at the same temperature should be equal. Thus, solely in terms of kinetic (rotational plus translational) energy it becomes awkward to understand why differing monatomic gases would possess different thermal conductivities. Unless it is based upon lighter molecules having higher mean velocities, hence requiring less time to travel a given distance, hence resulting in a quicker transfer of their kinetic energy. Conversely, polyatomic gases should have higher thermal conductivities due to all their vibrational energy, which enhances their ability to transfer energy.

Although measuring the thermal conductivity of gases is not an easy process, it is accepted that lighter gas molecules tend to have higher thermal conductivities. Furthermore, the more atoms a gas molecule has then the greater gas's the vibrational energy is at a given temperature, therefore the greater its thermal conductivity should be.

The above explains why argon possesses a low thermal conductivity hence is preferred for insulation purposes, e.g. used in thermal windows. I.e. argon being a relatively large monatomic gas will tend to be a relatively heavy slow moving molecule with no vibrational energy. Table 5.3 gives the thermal conductivity of some known gases<sup>1</sup>.

Table 5.3

Gas	Ar	Air	CO	CO2	H2	He	N2	O2
Kx10 <sup>3</sup>	42.71	67.21	64.44	68.05	428.1	362.2	63.02	71.79

The apparatus used to measure the thermal conductivity of gases is similar to that used for heat capacity, as was illustrated in Fig 5.2. It is accepted that such thermal conductivity apparatus does not allow for the best reproducibility. This author can envision issues such as:

- 1) A hot wire produces blackbody radiation that is not 100% thermal radiation.
- 2) A wire does not represent a flat surface wherein gas molecules can readily bounce off, in a simple discernable linear fashion.

Accordingly, the apparatus for calculating a gas's conductivity may require a rethink. Perhaps, in the future one might try having two parallel walls at different temperatures and then measuring the rate of heat transfer. In order for this setup to work, one would want to shield the hotter of the two walls from the gases in question, until the moment of measurement, e.g. use a sliding insulating wall. Of course this will only address 2) i.e. it will not address the above issue 1).

### ***Conclusions***

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Herein an understanding of heat capacities of gases and their application to heat transfer processes was investigated. Furthermore this can be considered as in part proof of the new perspective given concerning kinetic theory in Chapter 2.

Table 5.4: Accepted isometric ( $C_v$ ) and isobaric ( $C_p$ ) heat capacities and theoretical; $C_v = R(n''+1/2)$ [eqn (5.11)] and $C_p = R(n''+1/2) + R = R(n''+3/2)$ [eqn(5.12)]. Note: Accepted science heat capacities were calculated from the engineer values given in Table 5.5, which was obtained from Rolfe <sup>1</sup> exception being H <sub>2</sub> O <sub>2</sub> which is marked with * and was taken from Giguere <sup>7</sup> .						
Substance		$n''$	Accepted Empirical $C_p$ [J/(mol*K)]	Theoretical $C_p$ [J/(mol*K)]	Accepted Empirical $C_v$ [J/(mol*K)]	Theoretical $C_v$ [J/(mol*K)]
Helium	He	1	20.80	20.78	12.48	12.47
Neon	Ne	1	20.79	20.78	12.47	12.47
Argon	Ar	1	20.81	20.78	12.46	12.47
Xenon	Xe	1	20.58	20.78	12.47	12.47
Hydrogen	H <sub>2</sub>	2	28.83	29.09	20.52	20.78
Nitrogen	N <sub>2</sub>	2	29.14	29.09	20.82	20.78
Oxygen	O <sub>2</sub>	2	29.34	29.09	21.02	20.78
Nitric Oxide	NO	2	29.86	29.09	21.55	20.78
Water vapor	H <sub>2</sub> O	3	33.58	37.40	25.26	29.09
Carbon Dioxide	CO <sub>2</sub>	3	37.14	37.39	28.83	29.09
Sulfur Dioxide	SO <sub>2</sub>	3	39.78	37.39	31.46	29.09
Hydrogen peroxide*	H <sub>2</sub> O <sub>2</sub>	4	46.05	45.71	37.73	37.40
Ammonia	NH <sub>3</sub>	4	35.70	45.71	27.37	37.40
Methane	CH <sub>4</sub>	5	35.72	54.0	27.4	45.71
Ethylene	C <sub>2</sub> H <sub>4</sub>	6	43.54	62.325	35.24	54.02
Ethane	C <sub>2</sub> H <sub>6</sub>	8	52.65	78.95	44.35	70.64
Propylene	C <sub>3</sub> H <sub>6</sub>	9	63.92	87.26	53.82	78.95
Propane	C <sub>3</sub> H <sub>8</sub>	11	73.51	103.88	65.18	95.57
Benzene	C <sub>6</sub> H <sub>6</sub>	12	81.63	112.19	73.50	103.88
I-Butene	C <sub>4</sub> H <sub>8</sub>	12	85.68	112.19	77.09	103.88
n-butane	C <sub>4</sub> H <sub>10</sub>	14	97.42	128.81	89.10	120.50
Isobutane	C <sub>4</sub> H <sub>10</sub>	14	96.84	128.81	88.52	120.50
n-Pentane	C <sub>5</sub> H <sub>12</sub>	17	120.20	153.74	111.91	145.43
Isopentane	C <sub>5</sub> H <sub>12</sub>	17	119.99	153.74	111.69	145.43
n-Hexane	C <sub>6</sub> H <sub>14</sub>	20	143.06	178.67	134.78	170.36
n-Heptane	C <sub>7</sub> H <sub>16</sub>	23	165.94	203.60	157.62	195.29
Octane	C <sub>8</sub> H <sub>18</sub>	26	188.83	228.53	180.60	220.22

Table 5.5: Engineering table for adiabatic index compared to eqn 5.13:

The following is from the book: "Newthermodynamics: Say no to entropy" By Kent W Mayhew.

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$\gamma = C_p / C_v = (n''+3/2)/(n''+1/2)$ . Note: Data in first six columns was obtained from Rolle <sup>1</sup> .								
Substance		Mass per mole	$R''$	Engineer isobaric specific heat (25°C)	Engineer $C_v$ isometric specific heat (25°C)	Accepted $\gamma = C_p / C_v$	$n''$	$\gamma$ Eqn (5.13)
		[g/mole]	[J/(kg*K)]	[kJ/(kg*K)]	[kJ/(kg*K)]			
Helium	He	4.00	2079	5.196	3.117	1.667	1	1.667
Neon	Ne	20.18	412	1.030	0.618	1.667	1	1.667
Argon	Ar	39.94	208	0.521	0.312	1.668	1	1.667
Xenon	Xe	131.30	63	0.1568	0.095	1.667	1	1.667
Hydrogen	H <sub>2</sub>	2.02	4124	14.302	10.178	1.405	2	1.4
Nitrogen	N <sub>2</sub>	28.02	297	1.040	0.743	1.400	2	1.4
Oxygen	O <sub>2</sub>	32.00	260	0.917	0.657	1.396	2	1.4
Nitric Oxide	NO	30.01	277	0.995	0.718	1.386	2	1.4
Water vapor	H <sub>2</sub> O	18.02	462	1.864	1.402	1.329	3	1.29
Carbon Dioxide	CO <sub>2</sub>	44.01	189	0.844	0.655	1.288	3	1.29
Sulfur Dioxide	SO <sub>2</sub>	64.07	130	0.621	0.491	1.264	3	1.29
Ammonia	NH <sub>3</sub>	17.03	488	2.096	1.607	1.304	4	1.22
Methane	CH <sub>4</sub>	16.04	519	2.227	1.708	1.304	5	1.18
Ethylene	C <sub>2</sub> H <sub>4</sub>	28.05	297	1.552	1.256	1.236	6	1.15
Ethane	C <sub>2</sub> H <sub>6</sub>	30.07	277	1.751	1.475	1.188	8	1.12
Propylene	C <sub>3</sub> H <sub>6</sub>	42.08	198	1.519	1.279	1.187	9	1.11
Propane	C <sub>3</sub> H <sub>8</sub>	44.10	189	1.667	1.478	1.128	11	1.09
Benzene	C <sub>6</sub> H <sub>6</sub>	78.11	106	1.045	0.939	1.113	12	1.08
I-Butene	C <sub>4</sub> H <sub>8</sub>	56.11	148	1.527	1.374	1.111	12	1.08
n-butane	C <sub>4</sub> H <sub>10</sub>	58.12	143	1.676	1.533	1.093	14	1.07
Isobutane	C <sub>4</sub> H <sub>10</sub>	58.12	143	1.666	1.523	1.093	14	1.07
n-Pentane	C <sub>5</sub> H <sub>12</sub>	72.15	115	1.666	1.551	1.074	17	1.06
Isopentane	C <sub>5</sub> H <sub>12</sub>	72.15	115	1.663	1.548	1.074	17	1.06
n-Hexane	C <sub>6</sub> H <sub>14</sub>	86.18	96	1.660	1.564	1.062	20	1.05
n-Heptane	C <sub>7</sub> H <sub>16</sub>	100.20	83	1.656	1.573	1.053	23	1.04
Octane	C <sub>8</sub> H <sub>18</sub>	114.23	73	1.653	1.581	1.046	26	1.04

Rolle's<sup>1</sup> reference: Data Source J.F. Masi, Trans. ASME, 76:1067 (October, 1954): National Source of Standards (U.S.) Circ. 500, Feb 1952; "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Thermodynamic Research Center, Texas, A&M University; College Station, Texas.

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