

Chapter 7 Heat, Work, and the First Law of Thermodynamics

Calculate the electrical work for moving one mole of Na^+ ions across the membrane of a neuron.

Thermodynamics is the study of the interconversion of heat and work. In a thermodynamic study, a system undergoes a process involving energy transfers in the form of heat and work. We monitor the process by determining the change in the thermodynamic state of the system. The First Law states that the only way of changing the internal energy of system is through transfers of heat and work. There are many forms of work; the work of chemical change is our primary focus. One goal is to determine the amount of useful heat and work made available by a process. Another goal is to determine the equilibrium state of the system. The response of a system to transfers of heat and work depends on the properties of the system as specified by the heat capacity and equation of state of the system.

Chemical kinetics studies the approach to equilibrium, that is “how fast” a reaction runs. Thermodynamics studies the equilibrium state, which determines “how far” the reaction runs. Classical thermodynamics applies to the system at equilibrium. The final state of the system must be equilibrium. Knowing the changes in equilibrium position with changing conditions is important in learning how to control chemical processes for useful purposes.

7.1 Heat and Work

Heat and work are both transfers of energy. Heat and work cannot be stored in a bottle. Even though heat and work are linguistically nouns, in the scientific sense heat and work are verbs (or gerunds). Heat and work transfers occur during a process as energy is transferred from one object to another. Heat and work do not exist apart from the process. Thermal energy transfer is a commonly used alternative term for heat.

Heat and Work are Transfers of Kinetic Energy: Thermodynamics was developed before the notion of atoms and molecules was widely accepted by the scientific community. The theoretical development of thermodynamics does not require a molecular perspective; however, a molecular interpretation is often useful when considering new topics within the thermodynamic context.

Heat is the transfer of energy through random motions of molecules and **work** is the transfer of energy through organized motion. Consider a gas confined in a cylinder by a piston, with the gas defined as the system. When a thermal energy source comes in contact with the piston, collisions of the cold gas molecules with the hot walls of the piston increase the kinetic energy of the gas molecules. The increase in kinetic energy causes the gas molecules to move faster on average. The motion of the gas molecules is in random directions. Thermal energy is in the form of **random thermal kinetic energy**.

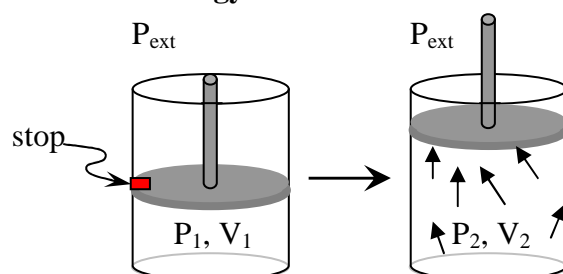


Figure 7.1.1: Work is done by the organized motion of atoms and molecules in the system.

Now consider transfer of energy as work. In Figure 7.1.1 the system does work against the surroundings. The work results from the net motion of the molecules in the upwards direction. Work is done by organized motion of molecules, all moving in the same direction on average.

We Interact with Our Environment Through Transfers of Heat and Work: Focusing on heat and work transfers may seem a bit foreign and restrictive. However, heat and work transfers are exactly the way that we sense and interact with the world around us. Take the sense of touch for example. When we touch things, objects feel hot or cold depending on whether energy, in the form of heat, is transferred to or from our finger tips. The other aspect of touch is how hard or soft something feels. Press your fingers on your desk and then press your fingers on your cheek. Pressing with your fingers is the equivalent of doing work on the object. The desk feels hard because for a given force from your finger tips, the volume change is small. Your cheek feels soft because for the same force, the volume change is much larger.

Now consider our other senses. Light is experienced either as radiant heat or through the work of chemical reactions. The sun feels warm on your skin, because energy is transferred to your skin through radiant heat transfer. Our eyes sense light through the chemical work of the *cis-trans* isomerization of the retinol in our retina.

So, we sense our environment through transfers of heat and work. How do we interact with the environment? When the air temperature is colder than our body temperature, we constantly lose energy to the surroundings in the form of heat. When the air temperature is warmer, energy in the form of heat is transferred into our bodies from the surroundings. We do work when we move objects, so the principle goal for athletes, musicians, and painters is the efficient production of work. When we think pleasant thoughts the nerve impulses result from the rapid switching of membrane potentials, thus doing electrical work. The membrane potentials are produced by the pumping of ions across the cell membranes of our neurons. Pumping ions across membranes requires chemical work. Of course, the energy for all these processes comes from the food we eat. The combustion of food in our mitochondria produces chemical work and some heat transfer. The work of chemical change, electrical work, work against surface tension, and work against elastic forces such as muscles are all types of **non-PV work**.

In a broader perspective, the efficient production of heat and work is critical to the continued health of our planet. Progress on global warming, in particular, involves the careful and thoughtful analysis of coupled thermodynamic systems. The efficiency of our global economy is a critical concern, since energy production has a huge impact on the environment. Energy is produced in the form of transportation fuels, fuels for heating, commodity chemicals, and agriculture. Food is in short supply in many areas of the globe, and competition for scarce resources accelerates environmental damage.

7.2 Thermal Energy Transfer—Heat Transfer

Heat Transfer can be Measured Through Changes in Temperature: The transfer of energy in the form of heat is often determined indirectly by the measurement of the change in temperature of an object:

$$q = C \Delta T \qquad \text{(cst. } C) \qquad 7.2.1$$

where the proportionality constant between heat transfer and temperature change is defined as the **heat capacity**, C . The change in temperature is given by the difference $\Delta T = T_2 - T_1$, where T_1 is the initial temperature and T_2 is the final temperature. The heat capacity is a fundamental

property of a substance. The units of heat capacity are J K^{-1} or equivalently $\text{J }^{\circ}\text{C}^{-1}$, since a change in temperature of 1 K is the same as 1°C . For a simple example, consider a hot stew. What should you eat first to avoid burning your tongue, the meat or the potatoe? Both the meat and potatoe start off at the same temperature and after contact with your tongue both end up at the same temperature. However, the wise eater chooses the meat first because meat has a smaller heat capacity than potatoe. The potatoe with the higher heat capacity transfers more energy to your tongue for a given temperature change. The heat capacity of water is atypically high, and potatoes have higher water content than meat.

Heat Transfer Depends on the Type of Process: There are two general types of systems. For open systems, processes can include transfers of matter or energy. For closed systems, processes can include transfers of energy, but not transfers of matter. We often depict closed systems as being in closed containers. However, for short periods of time, a cup of coffee on the desktop can be considered a closed system, as long as no significant evaporation occurs. If evaporation does occur the cup of coffee is an open system. In addition to the amounts of materials, processes often have other variables held constant.

Processes can occur at constant pressure, volume, or temperature. For example, any process open to the atmosphere is at constant pressure. A cup of coffee sitting on your desk is a constant pressure system. Examples of constant volume systems include autoclaves, kitchen canning jars, closed aerosol spray cans, and capped soda bottles. The most important chemical example of a constant volume system is a constant volume calorimeter bomb, which is used for determining internal energies of combustion. There are multiple ways of realizing a given type of process. For illustrative purposes, however, we often draw closed, constant pressure processes as being confined in a cylinder by a perfectly-sealing massless piston, with the piston in contact with the atmosphere, Figure 7.1.2. Constant volume conditions are maintained by a container with rigid walls.

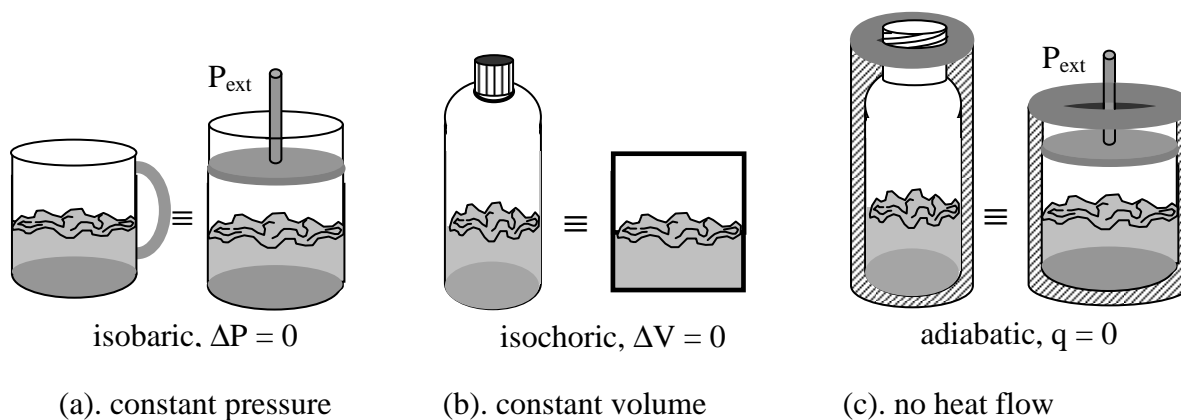


Figure 7.1.2: (a). A closed, constant pressure process is depicted as confined in a cylinder by a massless piston that is in contact with the atmosphere. A cup of coffee and a reaction in a beaker open to the atmosphere are examples. (b). Closed, constant volume systems are contained in sealed enclosures with rigid walls. (c). Adiabatic processes allow no heat transfer and are depicted in well-insulated containers. A thermos bottle open to the atmosphere is an example of a constant pressure adiabatic process.

The general types of processes have special names:

Constant pressure,	$\Delta P = 0$:	isobaric processes
Constant volume,	$\Delta V = 0$:	isochoric processes
Constant temperature,	$\Delta T = 0$:	isothermal processes
No heat transfer,	$q = 0$:	adiabatic processes

Processes in the human body are isobaric at ambient pressure and isothermal at 36.8°C, which is 310.0 K. Processes can be kept at constant temperature by being in contact with a constant-temperature **thermal reservoir**. Constant temperature water baths are examples of thermal reservoirs. Energy exchange between the reservoir and the system maintains equal temperatures. The surroundings often act as the thermal reservoir, giving $T = T_{\text{surr}}$. Barriers that allow thermal energy transfer are called **diathermal** barriers. Diathermal barriers allow the attainment of thermal equilibrium. For **adiabatic** processes no thermal energy is allowed to flow between the system and the surroundings, so $q = 0$. Adiabatic processes can be achieved through thermal insulation of the system or by doing the process quickly, before heat transfer takes place. An insulating barrier is also called an adiabatic barrier. Adiabatic processes can also occur at constant pressure, Figure 7.1.2c, or at constant volume.

The heat capacity depends on the conditions during the process. The heat capacity for a constant pressure process is different from the heat capacity for a constant volume process. At constant volume the heat transfer is given by:

$$q_v = C_v \Delta T \quad (\text{cst. } V \& C_v) \quad 7.2.2$$

and at constant pressure:

$$q_p = C_p \Delta T \quad (\text{cst. } P \& C_p) \quad 7.2.3$$

The subscripts specify that the energy transferred and the corresponding heat capacity is dependent on the **path** of the process, which in this case is either a constant volume path or a constant pressure path. Eqs. 7.2.1-7.2.3 assume a constant heat capacity. Heat capacities are functions of temperature for wide temperature ranges. For an infinitesimal transfer of energy:

$$\delta q = C dT \quad \delta q_v = C_v dT \quad \delta q_p = C_p dT \quad 7.2.4$$

in general, at constant volume, and at constant pressure, respectively. These last equations are integrated if the heat capacities are temperature dependent. The “ δ ” symbol for the infinitesimal is used to highlight the fact that the heat transferred is a function of the path. Solving these last equations for the heat capacities gives the definition of the constant volume and constant pressure heat capacities:

$$C_v \equiv \frac{\delta q_v}{dT} \quad C_p \equiv \frac{\delta q_p}{dT} \quad (\text{cst. } V \text{ or } P) \quad 7.2.5$$

Heat capacities are extensive properties of a substance. The constant pressure heat capacity of one gram of water is 4.179 J K⁻¹ and the heat capacity of 10.00 g of water is 41.79 J K⁻¹, at 25°C. An intrinsic measure of the heat capacity of a substance is given by the molar heat capacity:

$$C_{v,m} \equiv \frac{C_v}{n} \quad C_{p,m} \equiv \frac{C_p}{n} \quad (\text{cst. } V \text{ or } P) \quad 7.2.6$$

where n is the number of moles of the substance. Dividing by the amount normalizes the heat capacity for the size of the system (see Section 1.3). For solutions or substances with an unknown molar mass, the specific heat capacity is also useful:

$$C_{v,s} \equiv \frac{C_v}{w} \qquad C_{p,s} \equiv \frac{C_p}{w} \qquad (\text{cst. V or P}) \quad 7.2.7$$

where w is the mass of the substance or solution. The molar and specific heat capacities are intensive properties. Tables are available for heat capacities, especially those at constant pressure, in standard reference works.¹ A few examples are given in Table 7.2.1. The constant volume heat capacity of monatomic gases is $C_{v,m} = \frac{3}{2} R = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$ and the constant pressure heat capacity is $C_{p,m} = \frac{5}{2} R = 20.786 \text{ J K}^{-1} \text{ mol}^{-1}$ to within experimental error, except at low temperatures near absolute zero. A comparison of the heat capacities of CO, CO₂, and for the n -alkanes shows that the heat capacity increases with the number of atoms in the substance. Comparison of the solid, liquid, and gas forms for several substances is given in Table 7.2.2. The heat capacity of the liquid phase is greater than or equal to the solid, which shows that the liquid, while similar to the solid phase, has more motion and can store more energy. The heat capacity of the liquid is greater than the gas, which shows that some energy is stored in intermolecular forces thus increasing the heat capacity of the condensed phase.

Table 7.2.1: Constant Pressure Heat Capacities for a few Substances at 298.2 K and 1 bar.¹

Substance	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)	Substance	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
He (g)	20.786	CH ₄ (g)	35.309
Xe (g)	20.786	C ₂ H ₆ (g, ethane)	52.63
CO (g)	29.14	C ₃ H ₈ (g, propane)	73.51
CO ₂ (g)	37.11	C ₄ H ₁₀ (g, <i>n</i> -butane)	97.45

Table 7.2.2: Constant Pressure Heat Capacities for Different Phases.²

Substance	T (K)	Solid	Liquid	Gas
		$C_{p,m}$ (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)	$C_{p,m}$ (J K ⁻¹ mol ⁻¹)
Zn	693	30.	31.	
	1000		31.	20.8
Hg	234	28.	28.	
	500		28.	20.8
CO	68	52.9	60.2	
	80		60.7	28.9
H ₂ O	263	38.09	75.291	
	298		75.291	33.58
C ₃ H ₈ , propane	85	52.7	85.	
	298			73.5

Heat transfer is also conveniently measured for **resistive electrical heating**. Ohm's Law relates the voltage across a resistance R to the current flowing through the resistance: $V = IR$. The heat transferred from a wire or resistor with current flowing for time t is:

$$q = \int_0^t VI \, dt = \int_0^t I^2 R \, dt \quad 7.2.8$$

where V , I , and R are often time dependent. If the voltage and current are constant:

$$q = V I t = I^2 R t \quad (\text{cst. } V, I \text{ \& } R) \quad 7.2.9$$

Resistive heating is the most common reference or calibration method for heat flow. Resistive heating is also commonly called **Joule heating**. For example, the heat capacity of a metal can be simply measured by wrapping some resistance wire around the metal and measuring V , I , and t as the sample temperature increases. Eqs. 7.2.9 and 7.2.2 or 7.2.3 then give the heat capacity over the temperature range: $C_v = q_v/\Delta T$ or $C_p = q_p/\Delta T$, depending on whether the system is at constant volume or pressure. The heat capacity of a solution is often measured by immersing a resistor in the solution and passing a known current for a given period of time, using the same equations.

Heat capacities are functions of temperature; heat capacities increase with temperature for a given phase. Heat capacities are often approximated by a power series with four adjustable constants, a , b , c , and d :

$$C_{p,m} = a + b T + c T^2 + d T^3 \quad (\text{cst. } P) \quad 7.2.10$$

The coefficients, Table 7.2.3, are tabulated in standard reference works.¹ In many cases, the T^2 and T^3 terms are negligible and can be dropped. The power series is just the Taylor series expansion of the heat capacity as a function of the temperature, expanded around $T = 0$ K (see addendum Section 1.5). We often use power series expansions of thermodynamic quantities. Such expansions are useful because they provide an accurate determination of the variation of the quantity, but the expansions themselves are not necessarily theoretically insightful or unique. For example, many authors use the heat capacity expansion: $C_{p,m} = A + B T + C T^2$. Thermodynamics is a very practical science. The test of an equation is its usefulness. If Eq. 7.2.10 accurately expresses the temperature dependence of the heat capacity, then we will use it, even though we may not have a theoretical justification.

Table 7.2.3: Heat Capacity Coefficients for the Expansion: $C_{p,m} = a + b T + c T^2 + d T^3$ from 300 to 1800 K.³

Substance	a	b	c	d
	$\text{J K}^{-1} \text{mol}^{-1}$	$10^{-2} \text{J K}^{-2} \text{mol}^{-1}$	$10^{-5} \text{J K}^{-3} \text{mol}^{-1}$	$10^{-9} \text{J K}^{-4} \text{mol}^{-1}$
N_2 (g)	28.883	-0.157	0.808	-2.871
O_2 (g)	25.460	1.519	-0.715	1.311
H_2 (g)	29.088	-0.192	0.400	-0.870
CO (g)	28.142	0.167	0.537	-2.221
CO_2 (g)	22.243	5.977	-3.499	7.464
H_2O (g)	32.218	0.192	1.055	-3.593
NH_3 (g)	24.619	3.75	-0.138	–
CH_4 (g)	19.875	5.021	1.268	-11.004

Example 7.2.1

Here is a review question from General Chemistry, but one that highlights the important issues in thermal energy transfer. A 12.11 g piece of aluminum at 84.24°C is dropped into 100.0 mL of water at 20.22°C held in a Styrofoam cup. Assume the system is well insulated and neglect the energy lost to the Styrofoam cup and the thermometer. After equilibrium is attained, the temperature of the water is 21.85°C. Calculate the specific and molar heat capacity of aluminum.

Answer: The plan is to use the fact that $q_{\text{H}_2\text{O}} = -q_{\text{Al}}$. The heat lost by the aluminum and the heat gained by the water are necessarily equal in magnitude and opposite in sign because heat transfer is a process that transfers the given amount of energy from one object to another. The heat capacities are constant pressure heat capacities since the system is open to the atmosphere. The molar heat capacity of water is $75.291 \text{ J K}^{-1} \text{ mol}^{-1}$, Table 7.2.2. The density of water at 20.0°C, Table 2.2.1, is 0.9982 g mL^{-1} . The molar mass of water is 18.02 g mol^{-1} and of aluminum is 26.98 g mol^{-1} . The specific heat capacity of water is:

$$C_s(\text{H}_2\text{O}) = C_{p,m}(\text{H}_2\text{O})/\mathcal{M}_{\text{H}_2\text{O}} = 75.291 \text{ J K}^{-1} \text{ mol}^{-1} (1 \text{ mol}/18.02 \text{ g}) = 4.178 \text{ J K}^{-1} \text{ g}^{-1}$$

The mass of the water is $w_{\text{H}_2\text{O}} = d_{\text{H}_2\text{O}} V_{\text{H}_2\text{O}} = 0.9982 \text{ g mL}^{-1} (100.0 \text{ mL}) = 99.82 \text{ g}$.

The energy transferred as heat for the aluminum is given by:

$$q_{\text{AL}} = w_{\text{Al}} C_s(\text{Al})(T_2 - T_{1,\text{Al}})$$

The energy transferred as heat for the water is: $q_{\text{H}_2\text{O}} = w_{\text{H}_2\text{O}} C_s(\text{H}_2\text{O})(T_2 - T_{1,\text{H}_2\text{O}})$

Using $q_{\text{H}_2\text{O}} = -q_{\text{Al}}$ gives: $w_{\text{H}_2\text{O}} C_s(\text{H}_2\text{O})(T_2 - T_{1,\text{H}_2\text{O}}) = -w_{\text{Al}} C_s(\text{Al})(T_2 - T_{1,\text{Al}})$

Solving for the heat capacity for Al:

$$\begin{aligned} C_s(\text{Al}) &= -(w_{\text{H}_2\text{O}}/w_{\text{Al}}) C_s(\text{H}_2\text{O})(T_2 - T_{1,\text{H}_2\text{O}})/(T_2 - T_{1,\text{Al}}) \\ &= -(99.82 \text{ g}/12.11 \text{ g})(4.178 \text{ J K}^{-1} \text{ g}^{-1})(21.85^\circ\text{C} - 20.22^\circ\text{C})/(21.85^\circ\text{C} - 84.24^\circ\text{C}) \\ &= 0.8997 \text{ J }^\circ\text{C}^{-1} \text{ g}^{-1} = 0.8997 \text{ J K}^{-1} \text{ g}^{-1} = 0.900 \text{ J K}^{-1} \text{ g}^{-1} \end{aligned}$$

The result has only three significant figures since $\Delta T_{\text{H}_2\text{O}} = T_2 - T_{1,\text{H}_2\text{O}} = 1.63^\circ\text{C}$. The molar heat capacity is then:

$$C_{p,m}(\text{Al}) = C_s(\text{Al}) \mathcal{M}_{\text{Al}} = 0.8997 \text{ J K}^{-1} \text{ g}^{-1} (26.98 \text{ g mol}^{-1}) = 24.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

The system in this example is the water and aluminum. If the heat transferred to the Styrofoam cup and the thermometer were included in this calculation, then those transfers would be combined and called the “calorimeter” and then $q_{\text{H}_2\text{O}} + q_{\text{cal}} = -q_{\text{Al}}$ and $q_{\text{cal}} = C_{\text{cal}} \Delta T$. A separate calibration experiment is necessary to find the heat capacity of the calorimeter, C_{cal} . This calibration experiment is usually done using Joule heating with a resistor immersed in the calorimeter.

Example 7.2.2

A solution of 100.0 mL of 0.100 M HCl is held in an insulated flask fitted with a stirrer, electronic thermometer, and a resistance heater to form a constant pressure calorimeter. A current of 0.407 amp is passed through the heater for 45.6 s. The voltage across the heater is 4.064 V. The temperature increases by 0.172°C. Calculate the heat capacity of the calorimeter.

Answer: Using Eq. 7.2.9, the heat supplied by Joule heating is:

$$q = VIt = 4.064 \text{ V}(0.407 \text{ amp})(45.6 \text{ s}) = 75.42 \text{ J}$$

Using Eq. 7.2.5, assuming the heat capacity is constant over the temperature range, gives:

$$C_{\text{cal}} = q/\Delta T = 75.42 \text{ J}/0.172 \text{ K} = 438. \text{ J K}^{-1}$$

The heat capacity is labeled C_{cal} in these types of measurements to remind us that the heat capacity is for the solution, stirrer, thermometer, and heater combination. If a reaction is run in the calorimeter the heat transfer for the reaction is given by $q_{\text{p}} = -q_{\text{cal}} = -C_{\text{cal}} \Delta T$. The definition of the system for a reaction is just the bonds made and broken for the reactants and products.

The instruments that measure heat transfer are called calorimeters. **Calorimetry** is the experimental branch of thermodynamics. Calorimeters are available in an amazing variety of forms, but the underlying fundamentals are all based on the concept of heat capacity. To understand the operation of calorimeters, we also need to cover some issues in thermal transfer kinetics, which is a completely separate issue from the thermodynamics, but necessary and useful none-the-less.

The Kinetics of Thermal Transfer: Thermal energy can be transferred by conduction, convection, and radiation. Heat transfer is expressed as a flux in units of joules per unit area per second, $\text{J m}^{-2} \text{ s}^{-1}$, or equivalently in watts per unit area, W m^{-2} , since $1 \text{ W} = 1 \text{ J s}^{-1}$. **Thermal conductivity** can be expressed as a linear flux-force relationship. Referring to general pattern §2:

$$J_{\text{q}} = -\mathcal{K} \frac{dT}{dx} \quad 7.2.11$$

where \mathcal{K} is the thermal conductivity and dT/dx is the temperature gradient. Eq. 7.2.11 has direct analogies to diffusion, Eq. 2.3.4, and electrical conductivity, Eq. 2.5.5. The units of \mathcal{K} are $\text{J m}^{-1} \text{ K}^{-1} \text{ s}^{-1}$ (see Problem 2.19). **Thermal convective transfer** is also expressed analogously to mass transport; the thermal flux is proportional to the local velocity of the thermal transport medium, which commonly is air, water, or steam. **Radiative thermal energy transfer** is also expressed as a flux-force relationship, but radiative transfer is highly non-linear with temperature. The total flux, which is the radiative energy emitted per second per unit area by an object, is given by the Stefan-Boltzmann law:

$$J_{\text{q,radiative}} = \sigma T^4 \quad 7.2.12$$

where σ is the Stefan-Boltzmann constant, $5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$. A small temperature difference between a hot thermal source (like the sun) and an object results in a large rate of energy transfer, because of the fourth power dependence. In other words, every object, including every human, is constantly losing energy by the emission of infrared radiation. We will deal with radiative thermal energy transfer in more detail in Section 11.2.

Living systems are constantly exchanging thermal energy with their environment. For the human body in a resting state, conduction and convection account for 15% and radiation

accounts for 66% of the energy loss at 23°C. The remainder of the loss, 19%, is through evaporation of insensible perspiration, which amounts to 30 g water lost per hour.⁴ As a part of the convective losses, only 3% occurs during breathing. Insulated clothing on cool weather days drastically cuts thermal loss rates largely by immobilizing air; air in the absence of convection is a very good insulator.

Calorimeters are set up to avoid thermal transfer by convection and radiation. For example, a thermal shield often surrounds the sample cell. The temperature of the thermal shield is carefully controlled to match the sample temperature to minimize both radiative energy loss from the sample and convective air currents. Calorimeters that use a temperature controlled thermal heat shield are called adiabatic calorimeters.

Let's focus on heat conduction to find the temperature change for a system as a function of time. Consider the simplest case of a solution at temperature T in thermal contact with its surroundings at a constant temperature T_{surr} . We assume that the solution and the surroundings are well mixed and uniform in temperature, Figure 7.2.1.

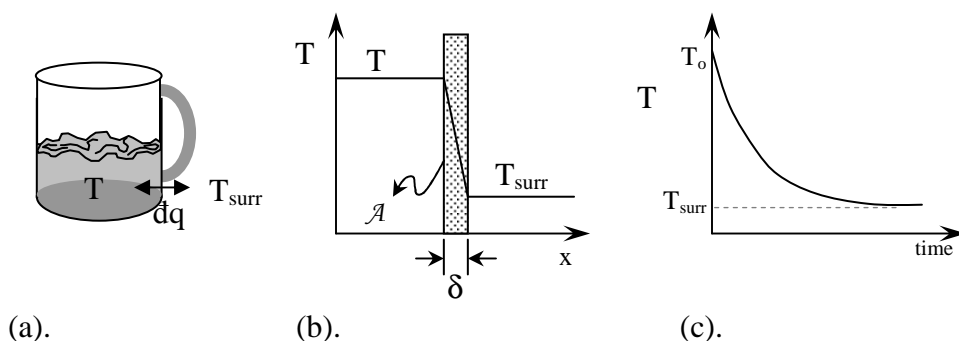


Figure 7.2.1: (a) Thermal transfer by conduction. The temperature of the solution and the surroundings are assumed to be uniform. (b). The interface has a linear temperature gradient of thickness δ . (c). The approach of the solution temperature to the surroundings is exponential.

Assume that the interface between the solution and the surroundings has thermal conductivity \mathcal{K} , a cross-sectional area \mathcal{A} , and a linear temperature gradient with thickness δ , giving $dT/dx = (T - T_{\text{surr}})/\delta$. The rate of thermal transfer is given by:

$$\frac{dq}{dt} = -\frac{\mathcal{K}\mathcal{A}}{\delta} (T - T_{\text{surr}}) \quad (\text{linear gradient}) \quad 7.2.13$$

(Also see Section 6.1.) The heat flow and temperature change are dependent on the heat capacity of the solution; taking the time derivative of Eq. 7.2.4 gives:

$$\frac{dq}{dt} = C_P \frac{dT}{dt} \quad 7.2.14$$

where C_P is the heat capacity of the solution and T is the temperature of the solution. The change in temperature of the solution is given from the heat transfer by equating Eqs. 7.2.13 and 7.2.14:

$$C_P \frac{dT}{dt} = -\frac{\mathcal{K}\mathcal{A}}{\delta} (T - T_{\text{surr}}) \quad (\text{linear gradient}) \quad 7.2.15$$

Dividing this last equation by the heat capacity and noting that $dT/dt = d(T - T_{\text{surr}})/dt$, since the temperature of the surroundings is assumed constant, gives Newton's Law of cooling:

$$\frac{d(T - T_{\text{surr}})}{dt} = - \left(\frac{\mathcal{K}\mathcal{A}}{\delta C_P} \right) (T - T_{\text{surr}}) \quad (\text{linear gradient}) \quad 7.2.16$$

This differential equation corresponds to simple exponential behavior. By general pattern **9I**, Eq. 1.3.24 gives the integrated form of Newtonian cooling as:

$$\int_{T_0}^T \frac{d(T - T_{\text{surr}})}{(T - T_{\text{surr}})} = - \int_0^t \left(\frac{\mathcal{K}\mathcal{A}}{\delta C_P} \right) dt \quad (\text{linear gradient}) \quad 7.2.17$$

$$(T - T_{\text{surr}}) = (T_0 - T_{\text{surr}}) e^{-\frac{\mathcal{K}\mathcal{A}}{\delta C_P} t} \quad (\text{linear gradient}) \quad 7.2.18$$

where T_0 is the initial temperature of the solution and T_{surr} is the temperature of the surroundings. In other words, the temperature of the solution approaches the temperature of the surroundings as an exponential function of time.

The rate of thermal transfer is a widely used concept. In the laboratory, the plot of temperature as a function of time is often an exponential function for calorimetric experiments (See Section 8.6). For a practical example, building insulation is characterized by an R-value, which is given by $R = \delta/\mathcal{K}$. Now that we have an understanding of thermal energy transfer, we can discuss one of the most commonly used forms of calorimetry.

7.3 Differential Scanning Calorimetry is a Highly Sensitive Measure of Heat Flow

Differential scanning calorimetry, DSC, monitors heat transfers associated with phase transitions and chemical reactions as a function of temperature. DSCs can be configured to work with samples sealed in sample pans or solutions in sample cells. In a DSC experiment, the temperature of the sample and a reference are increased at a constant rate. The change in temperature may induce various processes including phase transitions and thermal decomposition reactions. During the experiment, the temperature of the sample and the reference are kept equal by supplying heat to the sample and the reference independently. The difference in heat flow to the sample and the reference is recorded as a function of time, Figure 7.3.1. Since the temperature scan rate is constant, the time axis can be converted to a temperature axis. The reference for solid samples is an inert material such as alumina, or just an empty sample pan. For protein or nucleic acid studies in solution, the reference is usually just a buffer solution. The sample and reference cells are operated at constant pressure. Heat flow, \dot{dq}_p/dt , is given as J s^{-1} or equivalently watts. The heat flow difference between the sample and the reference is:

$$\Delta \frac{\dot{dq}_p}{dt} = \left(\frac{\dot{dq}_p}{dt} \right)_{\text{sample}} - \left(\frac{\dot{dq}_p}{dt} \right)_{\text{ref}} \quad 7.3.1$$

Dividing this equation by the contact area of the sample with its holder gives the differential heat flux. The output plot from the instrument is called a thermogram. The differential heat flow is positive for endothermic processes and negative for exothermic processes. In an endothermic process, heat is absorbed by the sample so that heat flow to the sample is higher than to the reference to keep the cells at equal temperatures. Examples of endothermic processes include helix-coil transitions in DNA, protein denaturation, dehydrations, reduction reactions, and some

decomposition reactions. DSC is the only technique that can completely determine the thermodynamic parameters involved in protein folding.⁵ Exothermic processes include crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions. A change in heat capacity caused by a phase transition or other chemical process is detected as a baseline shift, as indicated by $\Delta_{tr}C_p$ in Figure 7.3.1.

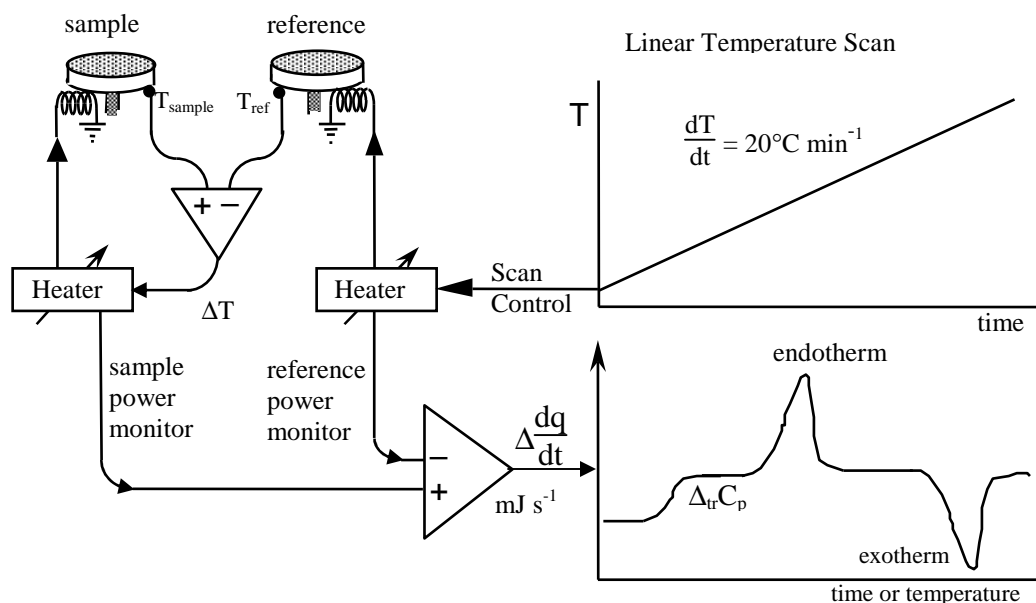


Figure 7.3.1: Differential scanning calorimeter. The triangles represent amplifiers that produce an output that is given by the difference in the inputs. The sample heater power is adjusted to keep the sample and reference at the same temperature during the scan. Typical temperature scan rates vary from 0.5 to 40°C min⁻¹. Few samples show all three features illustrated on the thermogram.

The instrument measures heat transfer, but remember from General Chemistry that the heat transfer at constant pressure is the enthalpy change for the process. We will develop the concept of enthalpy more completely in Section 7.8. For now, note that for a constant pressure process $\Delta \dot{dq}_p/dt = \Delta dH/dt$, so the DSC thermogram is a direct measure of both heat transfer and enthalpy changes.

Heat capacities and changes in heat capacity can be determined from the shift in the baseline of the thermogram, Figure 7.3.1. The temperature scan rate is:

$$\alpha = \frac{dT}{dt} \quad 7.3.2$$

Using Eq. 7.2.14, the heat capacity is given by the heat flow divided by the scan rate:

$$C_p = \left(\frac{\dot{dq}_p}{dT} \right) = \frac{\dot{dq}_p}{dt} \frac{dt}{dT} = \frac{(\dot{dq}_p/dt)}{\alpha} \quad (\text{constant P}) \quad 7.3.3$$

This equation can also be derived directly using the chain rule. In DSC the difference in the heat capacity of the sample and the reference is determined:

$$C_p(\text{sample}) - C_p(\text{ref}) = \Delta \left(\frac{\dot{d}q_p}{dT} \right) = \left(\Delta \frac{\dot{d}q_p}{dt} \right) \left(\frac{dt}{dT} \right) \quad (\text{constant P}) \quad 7.3.4$$

For a thermal transition, the integral of the area above the baseline gives the heat transfer for the transition, Figure 7.3.2. To prove this, first consider baseline subtraction. The heat transfer before the transition is just a function of the heat capacity of the sample and the reference from Eq. 7.2.14:

$$\Delta \frac{\dot{d}q_p}{dt} = C_{po}^{\text{sample}} \frac{dT}{dt} - C_p^{\text{ref}} \frac{dT}{dt} \quad (\text{constant P}) \quad 7.3.5$$

where C_{po}^{sample} is the heat capacity of the sample in its initial phase before the phase transition and C_p^{ref} is the heat capacity of the reference.

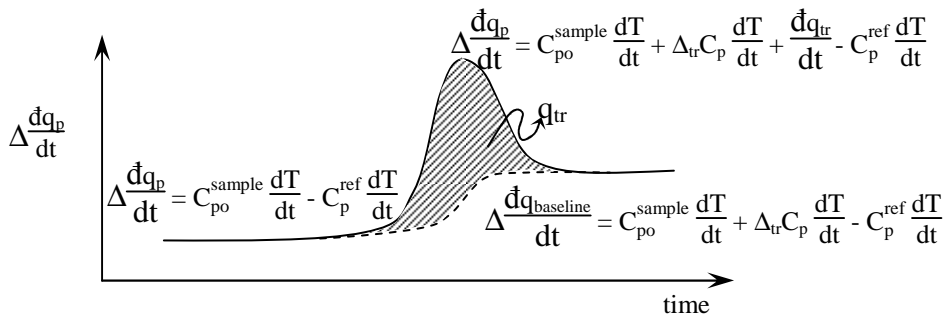


Figure 7.3.2: The solid line is a thermogram for a typical melting transition or thermal denaturation of a protein. The integral of the area above the baseline gives the heat transfer for the transition.

The phase transition is accompanied by a change in heat capacity, $\Delta_{tr}C_p$. For example, for a melting transition, $\Delta_{tr}C_p = C_p(\text{liquid}) - C_p(\text{solid})$, Table 7.2.2. The value of $\Delta_{tr}C_p$ is given by the baseline shift from before and after the phase transition, Eq. 7.3.4. Phase transitions are endothermic and require an additional heat transfer, $\dot{d}q_{tr}$. The total heat transfer during the transition is then given by:

$$\Delta \frac{\dot{d}q_p}{dt} = C_{po}^{\text{sample}} \frac{dT}{dt} + \Delta_{tr}C_p \frac{dT}{dt} + \frac{\dot{d}q_{tr}}{dt} - C_p^{\text{ref}} \frac{dT}{dt} \quad (\text{constant P}) \quad 7.3.6$$

where C_{po}^{sample} and C_p^{ref} are relatively weak functions of temperature compared to the heat transfer for the transition and the change in heat capacity for the transition. After the transition, the $\dot{d}q_{tr}/dt$ term is zero. The baseline before and after the transition can be smoothly interpolated:

$$\Delta \frac{\dot{d}q_{\text{baseline}}}{dt} = C_{po}^{\text{sample}} \frac{dT}{dt} + \Delta_{tr}C_p \frac{dT}{dt} - C_p^{\text{ref}} \frac{dT}{dt} \quad (\text{constant P}) \quad 7.3.7$$

where $\Delta_{tr}C_p$ increases from zero before the transition to the final change in heat capacity as the substance melts. Baseline subtraction then corresponds to subtracting Eq. 7.3.7 from 7.3.6:

$$\Delta \frac{\dot{d}q_p}{dt} - \Delta \frac{\dot{d}q_{\text{baseline}}}{dt} = \frac{\dot{d}q_{tr}}{dt} \quad (\text{constant P}) \quad 7.3.8$$

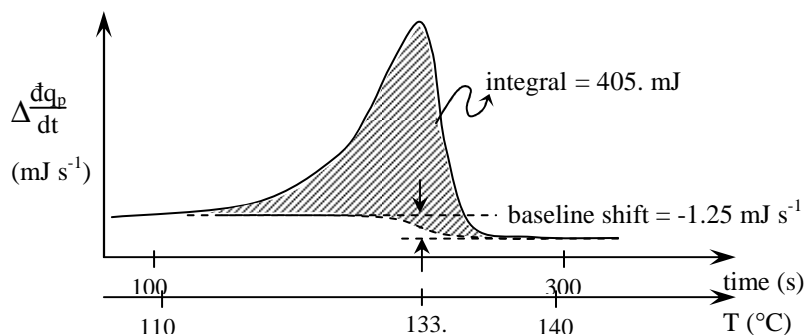
The heat flow after baseline subtraction is then just the heat transfer for the transition, \dot{dq}_{tr}/dt . The integral under the DSC peak, above the baseline, gives the total heat transferred and the enthalpy change for the process:

$$\int \frac{dq_{tr}}{dt} dt = q_{tr} = \Delta_{tr}H \quad (\text{constant P}) \quad 7.3.9$$

There are two types of DSC's, power compensation DSC's and heat flux DSC's. We focused on power compensation DSC's in this section. Heat flux DSC's place the sample and reference in a single oven and measure the temperature difference between the sample and reference. The heat flux is then given by Eq. 7.2.14. The heat capacity is calculated using Eq. 7.2.15. The thermal conductivities are calculated from calibration experiments using a standard sample with a known heat capacity.

Example 7.3.1:

The DSC thermogram for a sample from a commercial polyethylene milk bottle is shown below. The transition is the melting transition. The temperature scan rate was $20.0^\circ\text{C min}^{-1}$. The mass of the sample was 2.417 mg. The reference was an empty sample pan. Calculate the enthalpy of melting per gram and the change in specific heat capacity upon melting for polyethylene from the following thermogram.



Answer: The heat transfer for the melting transition is the enthalpy of melting:

$$\Delta_{tr}H = q_p = \frac{405. \text{ mJ}(1 \times 10^{-3} \text{ J/mJ})}{2.417 \times 10^{-3} \text{ g}} = 168. \text{ J g}^{-1}$$

We assume that the heat capacity of the reference changes slowly over the temperature range so that the baseline shift results entirely from the melting transition. The temperature scan rate is given as $20^\circ\text{C min}^{-1}$ or 20 K min^{-1} , since the centigrade and Kelvin degree size is the same. The change in heat capacity, with units conversion, for the transition is given by Eq. 7.3.3:

$$\Delta_{tr}C_p = -1.25 \text{ mJ s}^{-1}(1 \times 10^{-3} \text{ J/mJ})(1.00 \text{ min}/20.0 \text{ K})(60 \text{ s}/1 \text{ min}) = 3.75 \times 10^{-3} \text{ J K}^{-1}$$

The change of the specific heat capacity for the transition is the per gram quantity:

$$\Delta_{tr}C_{p,s} = 3.75 \times 10^{-3} \text{ J K}^{-1}/2.417 \times 10^{-3} \text{ g} = -1.55 \text{ J K}^{-1} \text{ g}^{-1}$$

The heat capacity is expected to increase on melting, Table 7.2.2. This observed decrease is dependent on processing conditions and the resulting degree of crystallinity of the polymer.

7.4 Work

There are many different forms of work. We first focus on the mechanical work of gas expansions and contractions, PV work. Every time you exhale, you are doing work against the external atmosphere. Chemical reactions that consume or produce gases, like respiration, also involve the exchange of energy with the surroundings through transfers of mechanical work. The general definition of work from physics is the energy change for displacement against a force, F . For an infinitesimal displacement, dx , the work is:

$$\delta w = F dx \quad 7.4.1$$

Integration gives:

$$w = \int_{\text{path}} F dx \quad 7.4.2$$

The path indication on the integral results because work, like heat transfer, is dependent upon the path of the process. For a constant force, the integral gives $w = F\Delta x$, Figure 7.4.1a. The change in energy of the surroundings from work transfer is $w_{\text{surr}} = -w$ and from thermal energy transfer is $q_{\text{surr}} = -q$. By convention, quantities without an explicit “surr” subscript are for the system.

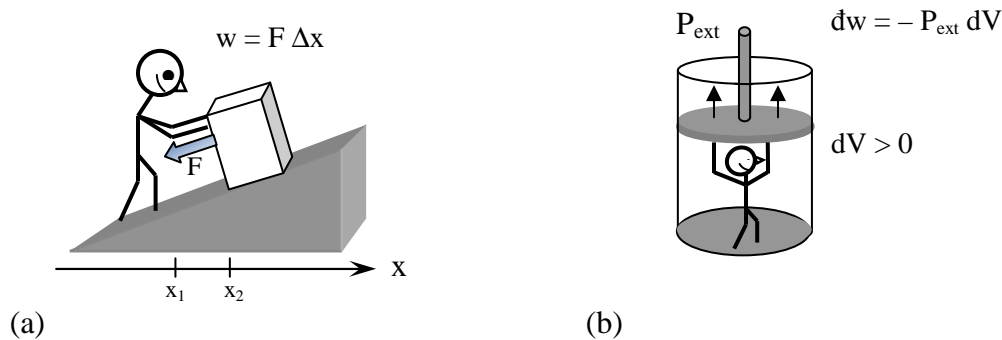


Figure 7.4.1: Work is done as a displacement against an opposing force. Picture yourself as the system. (a) For a positive displacement of a mass in the surroundings, your energy decreases, $w = F\Delta x$, where $F < 0$. (b). For an expansion, you push against the external pressure, $dV > 0$, doing work, thus lowering your energy, $\delta w < 0$.

Now consider the work done by changes in volume. Consider a gas confined in a cylinder by a massless piston with cross-sectional area A . If we both multiply and divide by the cross-sectional area in Eq. 7.4.1, the result is:

$$\delta w = \frac{F}{A} (A dx) = -P_{\text{ext}} dV \quad 7.4.3$$

where F/A is the external pressure, P_{ext} , and $(A dx)$ is the change in volume, dV . We need to be careful about the sign convention. We need to take the system as the point of reference. If the system does work, the change in volume is positive, $dV > 0$, and then $\delta w = -P_{\text{ext}} dV$ is negative. The system's energy must decrease to do the work. Is this sign convention consistent with the sign convention that we have chosen for heat transfer? From Eq. 7.2.1, if δq is positive the temperature of the system increases, showing that the energy of the system increases. Eqs. 7.2.1 and 7.4.3 have a consistent sign convention using the change in energy of the system as the point of reference. The pressure in Eq. 7.4.3 is the external pressure because work is done against an opposing force and the external atmosphere is responsible for the opposing force. Some examples will help make this distinction clearer and also show the path dependence of the integral of Eq. 7.4.3.

Consider the isothermal expansion of a gas, $P_1 > P_{\text{ext}}$. For the first example, assume that the gas expands against the ambient atmosphere, which is at a constant pressure P_{ext} , Figure 7.4.2a. Since the external pressure is constant the integral of Eq. 7.4.3 is just:

$$w = - \int_{V_1}^{V_2} P_{\text{ext}} dV = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \Delta V \quad (\text{cst. } T, P_{\text{ext}}) \quad 7.4.4$$

The process can be diagrammed in a plot of P versus V , Figure 7.4.2b. The pressure of the gas starts at a high value. When the stop is removed the pressure opposing the expansion is the constant external pressure. The area under the P - V curve is the negative of the work done by the system.

For the second example, consider the expansion of a gas against a vacuum, Figure 7.4.2c. The gas in the bulb on the left is defined as the system. The bulb on the left starts at a high pressure and the bulb on the right is evacuated, $P_{\text{ext}} = 0$. When the stopcock is opened the gas expands to fill both volumes. No work is done, because there is no opposing force since $P_{\text{ext}} = 0$.

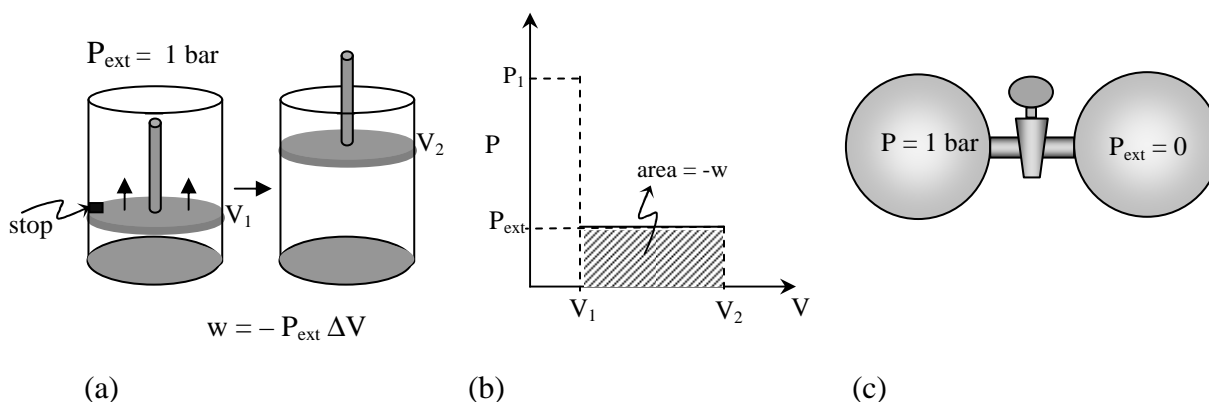


Figure 7.4.2: (a) Expansion against a constant external pressure equal to the ambient pressure. (b). The work done in a constant pressure expansion is the negative of the area under the P - V curve. (c). An expansion against a vacuum does no work because there is no opposing force.

A third example is a two step process, where the total external pressure is lowered by successively removing two weights from the top of the piston, Figure 7.4.3a. The final step is an expansion just against the external ambient pressure as in the first example. The change in

volume of the two-step process is the same as the constant pressure expansion; the final state in both cases is $P_2 = nRT/V_2$, where P_2 is the ambient pressure. However, the two-step process does more work because the intermediate step has a greater opposing pressure. The work is the negative of the sum of the two rectangular areas, Figure 7.4.3a.

A logical extension of the two-step process is a process that takes place by a sequence of many small steps. For the fourth example, imagine a bucket of sand attached to the piston, Figure 7.4.3.b. A hole is drilled in the bottom of the bucket to allow the grains of sand to drop from the bucket. The grains of sand replace the weights in the last example. As each grain of sand falls through the hole in the bottom of the bucket, the gas expands against the external pressure maintained by all the remaining grains of sand plus the ambient pressure. The initial and final volumes and pressures are the same as in the last example, since we arrange the mass of the sand to equal the mass of the two weights. However, this new process does more work, because at each stage of the expansion the system is expanding against the maximum possible pressure. Because the expansion takes place in very small steps, the internal pressure of the gas is equal to the total external pressure applied to the piston throughout the process, $P = P_{\text{ext}}$. Such an expansion does the maximum amount of work possible for an isothermal process for a given volume change. In the limit that the grains of sand become infinitesimally small, the system remains at equilibrium throughout the process.

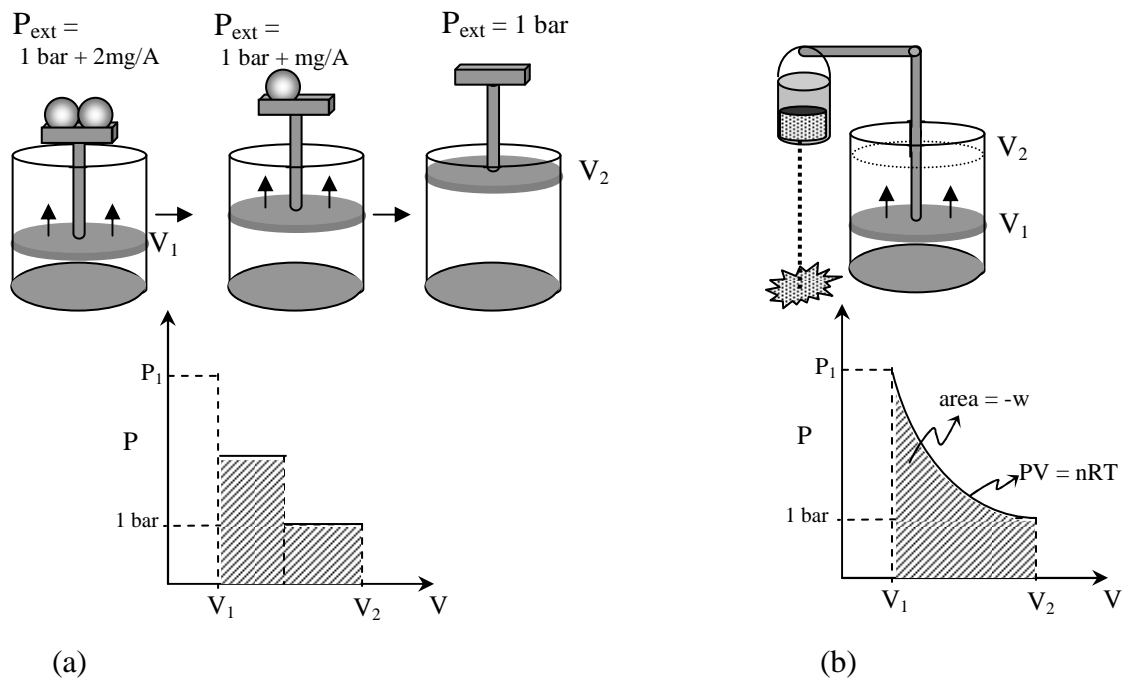


Figure 7.4.3: (a) A two-step expansion does more work for the same overall change in volume because the system expands against a greater external pressure in the first step. (b) The maximum work for an isothermal expansion is done in a sequence of reversible steps, where $P = P_{\text{ext}}$ at each step in the process.

If the process in Figure 7.4.3b occurs by a sequence of infinitesimal steps, each step is readily reversible; the change in volume for an infinitesimal decrease in the external pressure can be reversed by an infinitesimal increase in the pressure to return the system to its original state. In other words, if the hole in the bucket is plugged at any point during the expansion, the system is at equilibrium and remains at the given intermediate volume. Referring to Section 1.2, we see that this expansion is a reversible process. The value of this reversible isothermal expansion is that the process gives the maximum amount of work possible. Substituting $P = P_{\text{ext}}$ into Eq. 7.4.3 gives the work of an isothermal reversible process:

$$w = - \int_{V_1}^{V_2} P \, dV \quad (\text{reversible}) \quad 7.4.5$$

Because $P = P_{\text{ext}}$, the course of the process for an ideal gas follows the isotherm, $P = nRT/V$. The work of an isothermal reversible process for an ideal gas is then:

$$w = - \int_{V_1}^{V_2} nRT/V \, dV = - nRT \ln \frac{V_2}{V_1} \quad (\text{cst. } T, \text{ reversible}) \quad 7.4.6^\circ$$

Our four examples, Figures 7.4.2-7.4.3, show that work is dependent on the path of the process. Such a variable is called a path function. The general integral of a path function is shown with the explicit path dependence as:

$$w = - \int_{\text{path}} P_{\text{ext}} \, dV \quad 7.4.7$$

Our four examples, expansion against a constant pressure, expansion against a vacuum, a two-step process, and a reversible process, are different specifications of the path for the integral. Of these processes, you might think that the reversible process is quite impractical, since emptying a bucket of sand with infinitesimally small grains would take an infinite amount of time. No spontaneous process can be reversible. However, reversible processes give the limit of what is possible. Knowing the absolute best that we can do is often a useful tool in evaluating the efficiency of spontaneous processes.

7.5 Equations of State Specify the Mechanical Behavior of Systems

The integral in Eq. 7.4.5 shows that the work done in a reversible expansion is dependent on the properties of the substance. The ideal gas law is a limiting approximation. All gases approach ideal behavior as the density of the gas approaches zero, $n/V \rightarrow 0$. Gases deviate from ideal behavior at high densities and pressures and especially under conditions in which the gas can liquefy. A useful equation of state for gases under moderate conditions is the Van der Waals equation of state:

$$\left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT \quad 7.5.1$$

where a and b are adjustable coefficients that are determined by fitting to experimental data. The fact that the Van der Waals equation is a better representation of the properties of a gas than the ideal gas law is the only justification necessary for its use. However, a molecular interpretation of the form of the equation is particularly useful. Consider the $(V - nb)$ term. The Van der Waals b -coefficient is the excluded molar volume of the molecules. The ideal gas law corresponds to gas molecules with no molecular volume and no forces between the molecules. Real molecules

occupy space so that some of the volume of the container is excluded for the motion of the gas. The $(-nb)$ term is a correction to the actual volume of the container to give the volume an equivalent ideal gas would occupy.

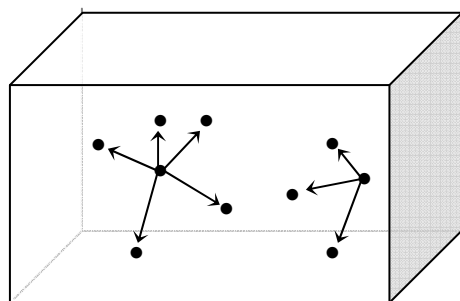


Figure 7.5.1: In the center of the container intermolecular forces balance. Near the walls of the container intermolecular forces are imbalanced providing a net decrease in pressure. The force of collisions with the wall is decreased.

The Van der Waals a -coefficient takes into account the intermolecular forces. Consider the collisions of gas molecules with the walls of a container, Figure 7.5.1. The pressure of the gas on the wall is given by:

$$P \sim (\text{force per collision})(\text{number of collisions in a given time}) \quad 7.5.2$$

At moderate densities intermolecular forces are attractive. In the center of the container, the intermolecular forces acting on a molecule are balanced because, on average, each gas molecule is surrounded uniformly by other molecules. However, the intermolecular forces near a wall are imbalanced giving a net force away from the wall. The force per collision for a real gas is smaller than for an ideal gas because of this imbalance. The correction for this imbalance should be a positive addition to the measured pressure to give the pressure that an equivalent ideal gas would exert. The imbalance in the forces near the wall is a function of the molar density of the gas. At higher density there are more molecules per unit volume and therefore more interactions “pulling” the colliding molecule away from the wall. The number of collisions in a given time is also a function of the molar density; more molecules in the gas provide more collisions per unit time with the wall. The net correction factor should then scale as the molar density squared, $\delta P \sim (n/V)^2$. The final corrected pressure is then given as $(P + a(n/V)^2)$.

Typical values for the Van der Waals coefficients are given in Table 7.5.1. The Van der Waals b -coefficients are comparable for a wide variety of molecules. The a -coefficients, on the other hand, vary by orders of magnitude. Intermolecular forces are strongly dependent on molecular size and structure. To judge the importance of the correction terms, consider one mole of propane at 1.000 bar and 298.2 K. Assuming ideal gas behavior gives the volume as 24.79 L. The correction to the volume from the Van der Waals equation is then just $(-nb) = (-1 \text{ mol})(0.0905 \text{ L mol}^{-1}) = -0.0905 \text{ L}$. The volume correction is only -0.4%. On the other hand, the correction for intermolecular forces using the a -coefficient is:

$$\left(a \frac{n^2}{V^2}\right) = 9.392 \text{ bar L}^2 \text{ mol}^{-2} \frac{(1 \text{ mol})^2}{(24.79 \text{ L})^2} = 0.01528 \text{ bar} \quad 7.5.3$$

or about a 1.5% correction compared to 1.000 bar. Even at such moderate conditions, propane shows significant deviations from ideal behavior.

Table 7.5.1^(DS): Van der Waals coefficients⁶

Molecule	a (bar L ² mol ⁻²)	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
Helium	0.03460	0.03415	0.02373
Hydrogen	0.02465	0.2432	0.02667
Nitrogen	1.3661	1.3483	0.03858
Oxygen	1.3820	1.3639	0.03186
Water	5.536	5.464	0.03049
Ethylene	4.6112	4.5509	0.05820
Ethane	5.5818	5.5088	0.06514
Propane	9.3919	9.2691	0.09049
Benzene	18.876	18.629	0.11974

(DS): Additional Values in the Appendix Data Section

Phase Diagrams Show the Behavior of Substances in Different Phases: The Van der Waals equation does a reasonable job of reproducing the behavior of gases, except at high densities and conditions in which the gas can liquefy. The plot of the P-V behavior of CO₂ is shown in Figure 7.5.2. The lines are plots of the pressure versus volume at constant temperature. Each line corresponds to a different constant temperature and is called an isotherm. For low densities, the behavior of the gas approaches ideal behavior. At high densities the gas can liquefy. Such P-V plots are called phase diagrams when more than one phase is possible. For example, consider a gas confined in a cylinder by a piston at high volume and temperature 22.4°C. We compress the gas and monitor the pressure at constant temperature. As the volume decreases, the pressure rises. As the volume decreases we reach point A where continued compression is possible without increasing the pressure; liquid is forming in the piston. The vapor pressure of a liquid is only a function of the temperature; the vapor pressure of CO₂ at 22.4°C is 60 bar. As long as both liquid and gas phases exist, any change in volume simply changes the relative amounts of gas and liquid in the piston. However, when all the gas is converted to liquid at point B, the barrel of the piston contacts only liquid. Further decreases in volume require large increases in pressure, since liquids are hard to compress. The isotherms in the liquid region of the phase diagram are steep.

The formation of the liquid corresponds to a sudden increase in density from the gas phase density and molar volume, $V_{m,\text{gas}}$, to the liquid phase density and molar volume, $V_{m,\text{liq}}$. The region between these two molar volumes is called a two phase region. Liquid and vapor are in equilibrium. As the temperature of the gas rises, the molar volumes of the gas and liquid approach each other. The point, at the top of the two phase region, where the gas and liquid molar volumes are equal is called the **critical point**. Above this temperature the gas can no longer liquefy. The pressure of the gas simply changes smoothly with changes in volume. The critical point corresponds to one specific temperature, pressure and molar volume, T_c , P_c , $V_{m,c}$. These critical properties are characteristic of the substance, Table 7.5.2.

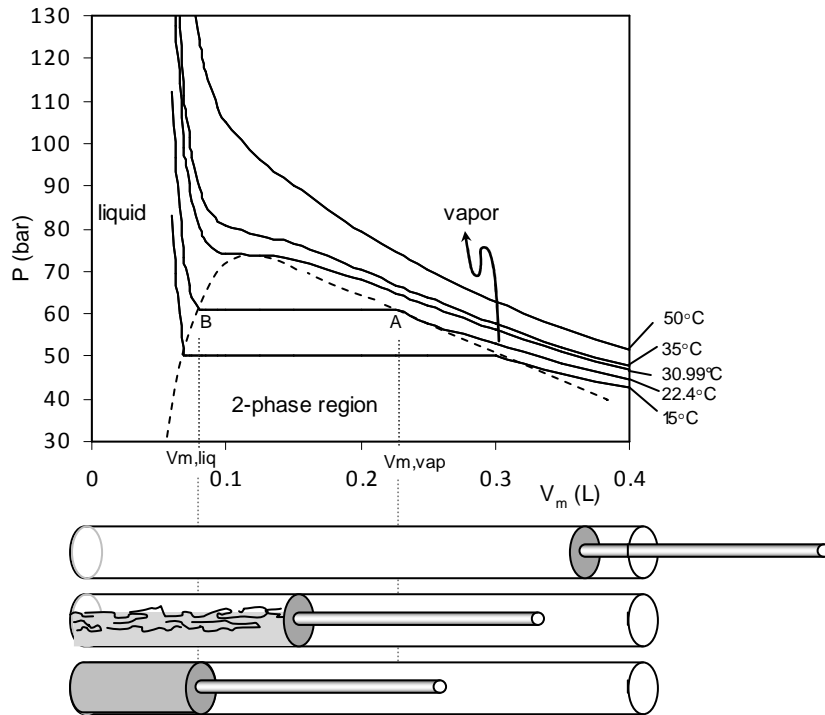


Figure 7.5.2: Phase diagram for CO_2 . The two phase region is outlined by the dashed line. Molar volumes in the two-phase region correspond to a mix of liquid and vapor at the vapor pressure of the liquid.

The Van der Waals equation of state does a reasonable job of reproducing the behavior of the system at temperatures above the critical point, Figure 7.5.3. The inflection point of the critical isotherm defines the critical point. However, the functional form of the Van der Waals equation is not capable of reproducing the sudden changes in the slope of the P-V curve at the edges of the two-phase region. Instead, the Van der Waals equation shows unphysical changes in pressure with volume in the two-phase region. In the middle of the two-phase region the slope of the P-V curve becomes positive leading to the prediction that the pressure would increase with increasing volume.

Table 7.5.2: Critical Constants.⁶

	P_c (bar)	P_c (atm)	$V_{m,c}$ (L mol^{-1})	T_c (K)
helium	2.2750	2.2452	0.05780	5.1950
nitrogen	34.000	33.555	0.09010	126.20
oxygen	50.427	50.768	0.07640	154.58
water	220.55	217.66	0.05595	647.126
carbon dioxide	73.843	72.877	0.09400	304.14
propane	42.477	41.922	0.2030	369.85

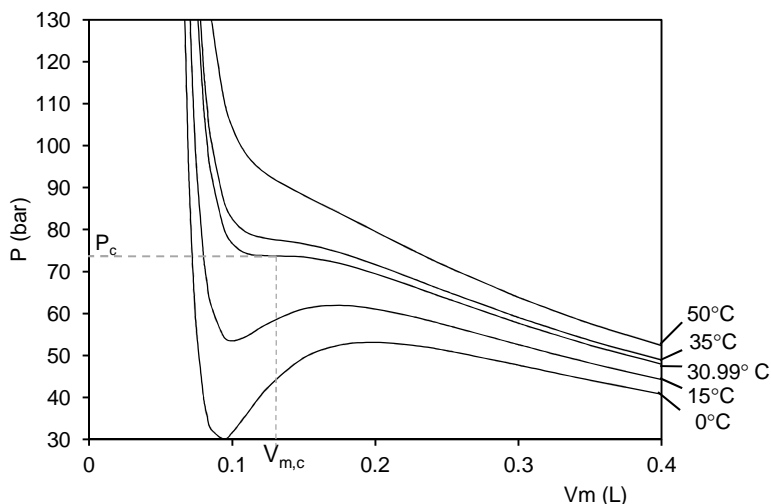


Figure 7.5.3: Van der Waals isotherms for CO₂. $T_c = 30.99^\circ\text{C}$. The portion of the isotherms with a positive slope are unphysical.

A gas above its critical temperature is called a **super-critical fluid**. Super-critical fluids have a smooth change in density as the volume is changed. This property makes supercritical CO₂ useful for drying biological samples for electron microscopy. Super-critical CO₂ is also useful for sample extraction for environmental sample preparation. This process is called **super-critical fluid extraction**, SFE. SFE is the method used to decaffeinate tea and coffee. Super-critical fluids can also be used as the mobile phase in chromatography for substances that are difficult to separate using normal gas chromatography and that are not amenable to liquid chromatography. The temperatures and pressures in mid-ocean hydrothermal vents are above the critical temperature and pressure of water. Geochemical models for mineral deposition under these extreme circumstances must treat water as a super-critical fluid.

The failure of the Van der Waals equation to model gases accurately at high density has led to the search for more accurate equations of state.

More Accurate Equations of State: The Redlich-Kwong equation of state is valid over a wider range of gas densities than the Van der Waals equation of state:

$$\left(P + A \frac{n^2}{T^{1/2}V(V+nB)} \right) (V - nB) = nRT \quad 7.5.4$$

The A and B coefficients are given in Table 7.5.3. While this equation of state is more accurate, the basic form of the equation is still not capable of predicting liquefaction (The equation is still basically a cubic equation in the volume).

There are many possible equations of state of varying accuracy. Each equation of state requires a separate table of coefficients, which is inconvenient. Johannes Diderik Van der Waals, in 1881, decided to ask if there is some universal behavior that characterizes all gases, instead of simply trying to derive new more accurate equations of state. A convenient method for finding the deviation from ideal behavior for a gas is to define the **compressibility factor**, z :

$$z \equiv \frac{PV}{nRT} \quad \text{giving} \quad PV = z nRT \quad 7.5.5$$

Table 7.5.3^(DS): Redlich-Kwong coefficients⁶

Molecule	A (bar L ² mol ⁻²)	A (atm L ² mol ⁻²)	B (L mol ⁻¹)
Helium	0.07991	0.07886	0.01645
Hydrogen	1.4333	1.4145	0.01848
Nitrogen	15.551	15.348	0.02674
Oxygen	17.411	17.183	0.02208
Ethylene	78.512	77.486	0.04034
Ethane	98.831	97.539	0.04515
Propane	183.02	180.63	0.06272
Benzene	453.32	447.39	0.08300

(DS): Additional Values in the Appendix Data Section

For an ideal gas the compressibility factor is one for all pressures and temperatures. For real gases the compressibility factor is less than one if attractive forces dominate the non-ideal behavior and greater than one if repulsive forces dominate. The compressibility factor for CO₂ at several different temperatures is shown in Figure 7.5.4a. Separate plots are necessary for different gases. However, Van der Waals noticed that plots of z as a function of P/P_c and T/T_c were almost identical for different gases. We define the **reduced** variables:

$$P_R \equiv P/P_c \quad V_R \equiv V/V_c \quad T_R \equiv T/T_c \quad 7.5.6$$

where P_c , V_c , and T_c are the critical parameters for the gas under consideration. The effect of the division by the critical parameters is to normalize the measured P , V , and T in a way that removes the particular characteristics of the gas. In other words, the critical parameters take into account the differences that make He different from O₂ and O₂ different from CO₂. The resulting reduced variables show the universal behavior of all gases. The result is called the **Law of Corresponding States**. A plot of z for a variety of gases as a function of the reduced pressure and temperature is shown in Figure 7.5.4b. Notice that to within 1% error all the gases follow the same equation of state over a wide range of conditions. Now we are getting somewhere; we only need one plot to describe the properties of many different gases.

Eq. 7.5.5 allows the compressibility factor to be calculated from experimental data. However, it is preferable to find a useful functional form for z instead of having to rely on plots such as Figure 7.5.4. What is the functional form for z ? Without additional information, at this point we simply assume that we can express z as a power series, just as we did for the heat capacity, Eq. 7.2.10. The compressibility factor is approximated as a power series in the molar density:

$$z = \frac{PV}{nRT} = 1 + B(T) \left(\frac{n}{V}\right) + C(T) \left(\frac{n}{V}\right)^2 + D(T) \left(\frac{n}{V}\right)^3 + \dots \quad 7.5.7$$

This equation is called the **virial equation**. The coefficients $B(T)$, $C(T)$, and $D(T)$ are called the **second virial coefficient**, **the third virial coefficient**, and **the fourth virial coefficient**, respectively. One advantage of the virial equation is that additional terms to higher order in the density can be added for better accuracy, if necessary. However, often the second and third virial coefficients are sufficient for all but the most extreme conditions. The virial coefficients are functions of temperature; extensive tables are available, Table 7.5.4.

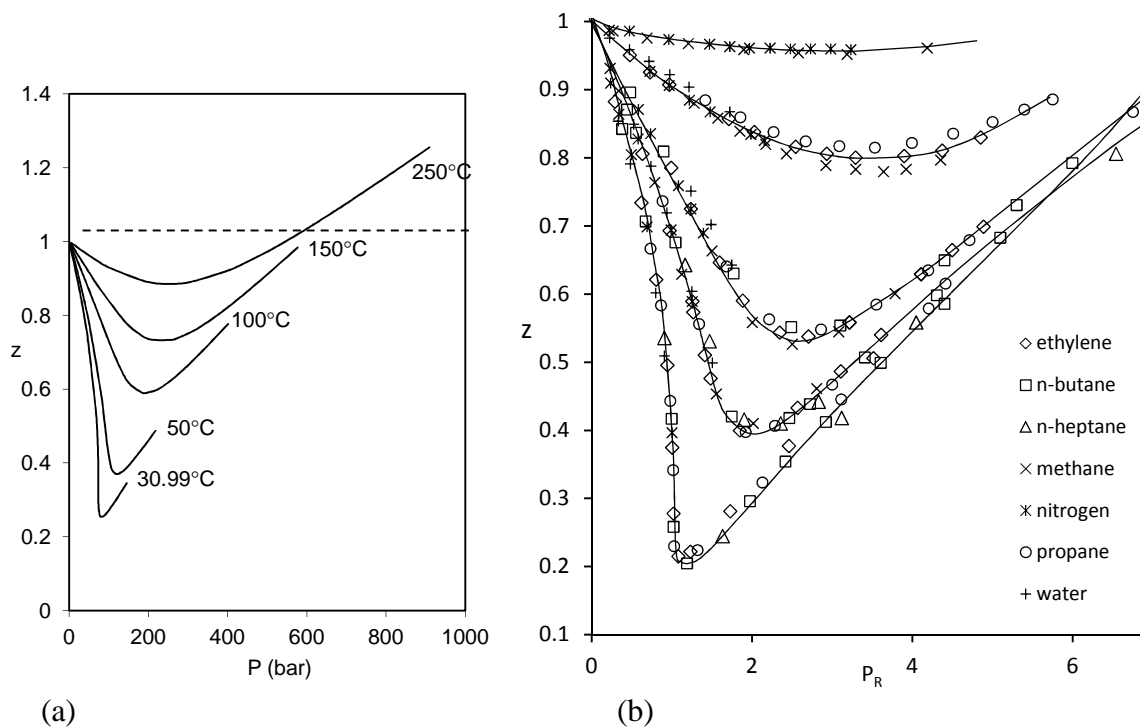


Figure 7.5.4: (a) Compressibility factor for CO_2 . (b). The compressibility factor versus reduced variables shows universal behavior for a wide variety of gases.

Table 7.5.4: Virial Coefficients at 298.15K.⁷

Molecule	B (L mol^{-1})	C ($\text{L}^2 \text{mol}^{-2}$)
Helium	0.0113	1.21×10^{-4}
Hydrogen	0.0141	3.50×10^{-4}
Nitrogen	-0.0045	0.001100
Oxygen	-0.0161	0.001200

The power series form of the virial equation is just an example of a Taylor series expansion. The expansion is around zero density, $x_0 = n/V = 0$, where the gas is ideal and z approaches 1. Comparing Eq. 7.5.6 to Eq. 1.5.16 gives the coefficients for the first two terms in the expansion:

$$f(x_0) = z|_{n/V=0} = 1 \quad \text{and} \quad \left(\frac{df}{dx}\right)_{x=x_0} = \left(\frac{dz}{d(n/V)}\right)_{n/V=0} = B(T) \quad (\text{cst. } T) \quad 7.5.8$$

$B(T)$ is called the second virial coefficient because it is the coefficient for the second term in the Taylor expansion. You will show in your homework that if the virial expansion is truncated to three terms, the virial coefficients and the Van der Waals coefficients are related by:

$$B(T) = b - \frac{a}{RT} \quad \text{and} \quad C(T) = b^2 \quad (D(T) = 0) \quad 7.5.9$$

The virial equation can also be written as a power series in the pressure by substituting $n/V = P/RT$ from the ideal gas law for the molar density into Eq. 7.5.6:

$$z = \frac{PV}{nRT} = 1 + \left(\frac{B(T)}{RT}\right)P + \left(\frac{C(T)}{(RT)^2}\right)P^2 + \left(\frac{D(T)}{(RT)^3}\right)P^3 + \dots \quad 7.5.10$$

Gases may be adequately described using many different equations of state. However, few accurate equations of state are available for liquids and solids. The mechanical behavior of condensed phases is often specified using the coefficient of thermal expansion and the isothermal compressibility. To discuss these parameters we first need to take a short detour to discuss partial derivatives. We return to the ideal gas law as a basis for our discussion.

7.6 Partial Derivatives Are Derivatives Taken One Variable at a Time

The ideal gas law for a closed system is a function of three variables, P , V , and T . For a closed system n is constant. We can display the ideal gas law as a series of plots. For example, consider the volume as a function of temperature at constant pressure, $V(T)$, giving the plot in Figure 7.6.1.a. The most convenient and consistent way to plot multi-variable functions is with the independent variable along the horizontal axis and the dependent variable on the vertical axis. The independent variable is the variable that you control. For example, for V as a function of T , you might control the temperature in the laboratory using a hot plate. The dependent variable is the measured response of the system. The most consistent way to rearrange the ideal gas law to coincide with the choice of independent and dependent variables is to isolate the dependent variable on the left-hand side of the equation:

$$V = \left(\frac{nR}{P}\right)T \quad 7.6.1^\circ$$

We can think of this last equation as being in the form of a straight line with slope (nR/P) and zero intercept. Equivalently we can find the slope using the partial derivative:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad (\text{closed}) \quad 7.6.2^\circ$$

The dV and dT from single-variable derivatives are replaced by ∂V and ∂T to remind us that we are taking the derivative with respect to T while holding all the other variables constant. We list, as subscripts, all the variables that are being held constant. Except for the changes in notation, a partial derivative is just like a regular derivative. We take the derivative with respect to one independent variable at a time.

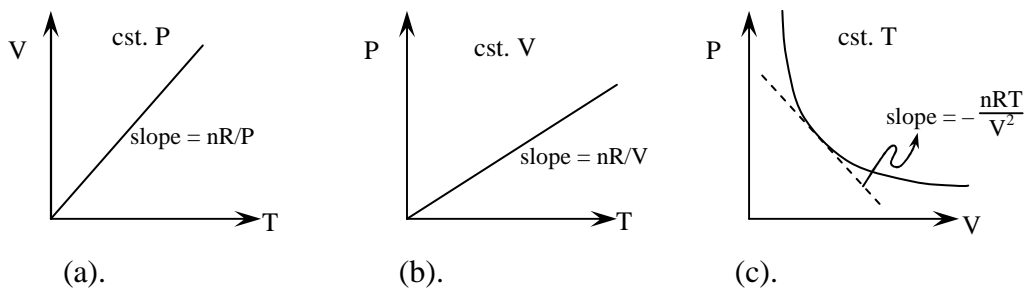


Figure 7.6.1: The ideal gas law with (a) V versus T at constant P , (b) P versus T at constant V , and (c) P versus V at constant T . The curve in this last plot is an isotherm.

As a second example, consider the pressure plotted as a function of the temperature at constant volume, Figure 7.6.1b. This plot corresponds to P as the dependent variable and T as the independent variable with:

$$P = \left(\frac{nR}{V}\right) T \quad 7.6.3^\circ$$

This plot has the slope (nR/V) , which we can also find using the partial derivative:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad (\text{closed}) \quad 7.6.4^\circ$$

In the plot of P versus V at constant temperature, Figure 7.6.1c, the slope is harder to determine. Isolating the dependent variable, P , on the left gives:

$$P = (nRT) \frac{1}{V} \quad 7.6.5^\circ$$

This function defines the isotherm in the plot. The partial derivative that gives the slope of the P versus V plot is:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} \quad (\text{closed}) \quad 7.6.6^\circ$$

Example 7.6.1:

Find the partial derivative of P as a function of V for an isothermal process with a Van der Waals gas.

Answer: We first need to rearrange Eq. 7.5.1 to isolate the dependent variable on the left:

$$P = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$$

We then hold n and T constant and take the derivative. Consulting Addendum 1.5, we find:

$$\frac{d(1/x^n)}{dx} = \frac{-n}{x^{n+1}}$$

Then the partial derivative is given by:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + \frac{2an^2}{V^3}$$

The mechanical behavior of liquids, solutions, and solids is often defined in terms of partial derivatives with respect to the volume.

The Coefficient of Thermal Expansion and the Isothermal Compressibility Describe the Mechanical Behavior of Condensed Phases: Consider that the volume of a substance is a function of temperature and pressure, $V(T,P)$. For infinitesimal changes in temperature and pressure the change in volume is given by:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (\text{closed}) \quad 7.6.7$$

This expression is called the **total differential** of the volume. The first term on the right, for example, can be interpreted as simply the change in volume for very small changes in temperature; the slope with respect to change in temperature is the partial derivative $(\partial V/\partial T)_P$. The second term is the analogous change in volume for very small changes in pressure, dP . (Please see the addendum, Sec. 7.11, for more information on partial derivatives and the total differential.) The partial derivatives in Eq. 7.6.7 express fundamental properties of the system. However, since V is extensive, the partial derivatives depend on the size of the system. To tabulate information on a variety of substances, the fractional or relative changes are used. The **coefficient of thermal expansion** is defined as:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{closed}) \quad 7.6.8$$

The relative changes are intensive; they are independent of the size of the system, so they express an intrinsic property of the system. Multiplying α by 100% gives the volume change on a percentage basis. The coefficient of thermal expansion is also called the **isobaric thermal expansivity**, since the derivative is taken at constant pressure. The units of α are just K^{-1} . The partial derivative of the volume with respect to pressure is also tabulated as a relative change:

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (\text{closed}) \quad 7.6.9$$

which is called the **isothermal compressibility**. The negative sign is included because the change in volume with increasing pressure is negative, thus making κ_T overall positive and easier to tabulate, Table 7.6.1. The units are bar^{-1} or atm^{-1} . Note that some texts use β for the symbol, $\kappa_T = \beta$. Both α and κ_T are often called the **basic derivatives**, since all the mechanical derivatives of a system can be expressed in terms of α and κ_T . Substituting the definitions in Eqs. 7.6.8 and 7.6.9 into the total differential, Eq. 7.6.7 gives:

$$dV = V \alpha dT - V \kappa_T dP \quad (\text{closed}) \quad 7.6.10$$

Table 7.6.1^(DS): The coefficient of thermal expansion and isothermal compressibility at 25°C.

Substance	α (K^{-1})	κ_T (bar^{-1})
Benzene	12.4×10^{-4}	90.9×10^{-6}
Water	2.57×10^{-4}	45.3×10^{-6}
Cu	0.500×10^{-4}	0.775×10^{-6}
Diamond	0.030×10^{-4}	0.185×10^{-6}

(DS): Additional Values in the Appendix Data Section

Eq. 7.6.10 is easily integrated to find the change in volume for any process in a closed system. Before we proceed however, it is important to verify that α and κ_T do give everything we need to know about mechanical behavior. For example, how do we find the change in pressure for a change in temperature for a constant volume process?

$$\left(\frac{\partial P}{\partial T}\right)_V = ? \quad (\text{closed}) \quad 7.6.11$$

It is not obvious that this derivative can be expressed in terms of α and κ_T . The key to finding the relationship is to focus on the constant volume constraint. For a constant volume process the total differential of the volume is zero; from Eq. 7.6.7:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = 0 \quad (\text{closed}) \quad 7.6.12$$

Subtracting the temperature dependent term from both sides of the equation gives:

$$\left(\frac{\partial V}{\partial P}\right)_T dP = -\left(\frac{\partial V}{\partial T}\right)_P dT \quad (\text{closed}) \quad 7.6.13$$

We can then solve for the differential of the pressure:

$$dP = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} dT \quad (\text{closed}) \quad 7.6.14$$

To find the partial derivative in Eq. 7.6.11 we “divide” by dT and specify constant volume conditions:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad (\text{closed}) \quad 7.6.15$$

We can relate these partial derivatives to α and κ_T by dividing the numerator and denominator of this expression by the volume:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa_T} \quad (\text{closed}) \quad 7.6.16$$

The result is that the behavior of the system can be expressed as a function of only α and κ_T . Also note that this derivation is an example of a key partial derivative relationship, called the **Euler Chain Relationship** that we will use many times. Partial derivative manipulations are summarized in the Addendum. Now that we know the importance of the basic derivatives, we can integrate the relationships for finite changes.

The approach to integrating the basic derivatives depends on the size of the temperature and pressure changes and the desired accuracy. We will illustrate this issue for small changes,

moderate changes, and very large changes. Consider first small temperature changes at constant pressure. For small changes the volume doesn't change much and we can set the volumes on the right-hand side of Eq. 7.6.10 to the initial volume of the system, $V \approx V_o$. For an isobaric process Eq. 7.6.10 reduces to:

$$dV = V \alpha dT \quad (\text{closed, cst. P}) \quad 7.6.17$$

Integrating from the initial temperature T_o and initial volume V_o to the final temperature T and final volume V :

$$\int_{V_o}^V dV = \int_{T_o}^T V_o \alpha dT \quad (\text{closed, cst. P}) \quad 7.6.18$$

Assuming V_o and α are constants, the integrals give:

$$(V - V_o) = V_o \alpha (T - T_o) \quad \text{or} \quad \Delta V = V_o \alpha \Delta T \quad (\text{closed, cst. P \& } \alpha, \text{ small } \Delta T) \quad 7.6.19$$

We can also add V_o to both sides of the equation to give:

$$V = V_o + V_o \alpha (T - T_o) \quad (\text{closed, cst. P \& } \alpha, \text{ small } \Delta T) \quad 7.6.20$$

In other words, in this approximation the volume is a linear function of the temperature.

For moderate changes in temperature, we can no longer assume that the volumes on the right-hand side of Eq. 7.6.10 are constant. For moderate changes in temperature we can use a successive approximations approach. Substituting Eq. 7.6.20 into Eq. 7.6.17 gives the following approximation:

$$dV = [V_o + V_o \alpha (T - T_o)] \alpha dT \quad (\text{closed, cst. P, moderate } \Delta T) \quad 7.6.21$$

Integration then gives:

$$\int_{V_o}^V dV = \int_{T_o}^T V_o \alpha dT + \int_{T_o}^T V_o \alpha^2 (T - T_o) dT \quad (\text{closed, cst. P, moderate } \Delta T) \quad 7.6.22$$

which integrates to:

$$(V - V_o) = V_o \alpha (T - T_o) + \frac{V_o \alpha^2}{2} (T - T_o)^2 \quad (\text{closed, cst. P \& } \alpha, \text{ moderate } \Delta T) \quad 7.6.23$$

Notice that the first term is just what we found for a small change in temperature. The second term can be thought of as a correction term. Another way of looking at this last equation is that we have found the first two terms in the Taylor series expansion of the volume change.

For large changes in temperature, we can take a more accurate approach. Notice that Eq. 7.6.17 is in the form of a *simple exponential process*, general pattern **9I**, which we used so many times in the chapters on kinetics. Separating variables and integrating gives:

$$\int_{V_o}^V \frac{dV}{V} = \int_{T_o}^T \alpha dT \quad (\text{closed, cst. P}) \quad 7.6.24$$

Using general pattern **9I** and assuming α is constant, we can write:

$$V = V_o e^{\alpha(T-T_o)} \quad (\text{closed, cst. P \& } \alpha) \quad 7.6.25$$

You might wonder, if we can do the integral exactly why we bothered with the approximations? Eqs. 7.6.19 or 7.6.20 are often good enough for many purposes and display simple linear behavior. Eq. 7.6.23 is better and is in a power series form, which is often convenient for calculations. Eq. 7.6.25 is best since it is applicable over a wide range of temperatures, however, the exponential form may be cumbersome for some derivations and the accuracy of the equation may not be worth the extra complexity. This “good, better, best” relationship also applies, for example, to the accuracy of the ideal gas law, the Van der Waals equation of state, and the virial equation of state. We often choose to use approximations simply for ease of use, if the situation warrants.

Example 7.6.2:

Express the following partial derivative in terms of α and κ_T :

$$\left(\frac{\partial P}{\partial V}\right)_T = ?$$

Answer: Notice that we can invert the partial derivative:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} \quad 7.6.26$$

Solving Eq. 7.6.9 for the new partial derivative: $\left(\frac{\partial V}{\partial P}\right)_T = -V \kappa_T$ 7.6.27

Substitution back into Eq. 7.6.26 gives:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{V \kappa_T} \quad 7.6.28$$

Example 7.6.3:

Even though we normally use α and κ_T to find changes in volume for condensed phases, it is instructive to find α and κ_T for an ideal gas. Find α and κ_T for an ideal gas.

Answer: From Eqs. 7.6.8 and 7.6.2°:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \left(\frac{nR}{P}\right)$$

Using the ideal gas law in the form $PV = nRT$ and substituting into the denominator of this last equation gives:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}$$

From Eq. 7.6.9 for κ_T , we need to find $(\partial V/\partial P)_T$. For the ideal gas $V = nRT/P$ and

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{nRT}{P^2}$$

Substitution back into the definition for κ_T and substituting $PV = nRT$ in the denominator gives:

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{V} \left(\frac{nRT}{P^2}\right) = \frac{1}{P}$$

The equation of state for gases and alternatively α and κ_T for condensed phases provide all the information we need to determine the mechanical behavior for any system. For example, consider a small change in temperature for a liquid or a solid in contact with the surroundings. This expansion is at constant pressure with $P = P_{\text{ext}}$. The work done, substituting Eq. 7.6.19 into Eq. 7.4.5, results in an important equation in oceanography and atmospheric chemistry:

$$w = -\int_{V_1}^{V_2} P \, dV = -P \Delta V = -PV_o \alpha \Delta T \quad (\text{cst } P \& \alpha, \text{ small } \Delta T) \quad 7.6.29$$

7.7 The Zeroth Law of Thermodynamics Allows the Empirical Definition of Temperature

We have been using the concept of temperature without carefully defining what we mean by the term. In this section we briefly introduce some of the important concepts surrounding the definition of an empirical temperature scale. For a moment, please forget that we know anything about the concept of temperature.

The hotness of an object is a sensation we directly experience through touch. We need to develop a corresponding thermodynamic measurement that correlates with our sensation of hotness. Thermometers are an empirical way of defining this variable. But, how can we be sure that thermometers measure hotness in a meaningful way? The basis for the development of the concept of temperature and of thermometers is the **Zeroth Law** of thermodynamics.⁸ Consider two objects, A and B, that are brought into thermal contact. By thermal contact we mean the objects can exchange energy through a diathermal barrier to achieve thermal equilibrium. Our experience tells us that at thermal equilibrium, the two objects will be equally hot. Now consider a third object, C. The Zeroth Law states that if A and B are found to be at thermal equilibrium and if B and C are found to be in thermal equilibrium, then A and C must also be in thermal equilibrium. In addition, since we can use the hotness of an object to judge thermal equilibrium, we can state that if A and B are equally hot, and B and C are equally hot, then A and C must be equally hot. We can now use object C as a thermometer. The hotness as measured by object C can be used to compare any two systems, even if the two systems are very different in size and composition. But how can we physically measure hotness? Are pressure and volume measures of hotness?

Consider a gas, confined in a cylinder by a piston, in thermal equilibrium with the surroundings. Boyle's Law establishes that the PV_m product of an ideal gas is a constant for a gas in thermal equilibrium with its surroundings:

$$PV_m = \text{cst} \quad (\text{ideal gas, thermal equilibrium}) \quad 7.7.1^\circ$$

with V_m the molar volume. We can vary the pressure and volume of the gas over a wide range of values, while keeping PV_m equal to a constant. But as long as the gas remains in thermal

equilibrium with the surroundings, we know that the gas stays at the same hotness. So, separately neither pressure nor volume measure hotness. However, we know that the product of pressure and volume, PV_m , always increases as the gas gets hotter. The constant in Boyle's Law is small for cold systems and large for hot systems. We can use any measurement that correlates with our sense of hotness as a thermometer; the expansion of air was the basis for the first thermometer. Then using an ideal gas as a thermometer, we can define the PV_m product as being proportional to the empirical temperature, θ :

$$PV_m = \text{cst} = R(\theta + C) \quad (\text{ideal gas}) \quad 7.7.2^\circ$$

where the proportionality constant, R , and the constant C must be fixed by experiment. Eq. 7.7.2° provides an equation for the temperature in two unknowns. To complete the definition of the empirical temperature scale we must choose two arbitrary fixed points, giving two equations in two unknowns from which we can calculate R and C . The absolute temperature scale is most convenient because then we set $C = 0$ and $\theta = T$ in kelvins. The constant R is then evaluated by arbitrarily choosing the freezing point of water at 1 atm as 273.15 K, which is the basis of our calculations for R in Section 1.3.

Carefully measuring the pressure and volume of a gas is not a particularly convenient or portable means of measuring temperature. So subsequent to the development of the gas thermometer, alcohol in glass and then mercury in glass thermometers were developed and calibrated against the ideal gas thermometer. Any working substance or property can be used as a thermometer, as long as the equation of state is accurately known. With temperature defined we can now return to the Zeroth Law of thermodynamics and state that if systems A and B are at the same temperature and if systems B and C are at the same temperature then systems A and C will be at the same temperature. Any of the three systems, A, B, or C, may be chosen as a thermometer. The empirical definition of temperature is essentially: "temperature is the property measured by a thermometer." Temperature is the necessary variable for assessing if two systems are at thermal equilibrium. The relationship of the empirical temperature to P and V is established experimentally by the equation of state of the substance. We will develop the more fundamental and direct thermodynamic definition of temperature in Chapter 10 when we introduce the concept of entropy. (See also Problem 17 for more information about the ideal gas thermometer).

7.8 Heat and Work Are Path Functions, but Internal Energy Is a State Function

We depend on thermodynamic systems to heat our homes, to make electricity, to power our automobiles. The heat and work available from thermodynamic processes power our society and drive processes in nature, including chemical change. How much heat and work are available from a thermodynamic process? We need to do a careful accounting of all the energy effects to be able to understand and predict the outcome of different processes. Let's start with several simple illustrative processes. Consider a capped, uninsulated container of hot coffee, which is hotter than the surroundings, Figure 7.8.1a. Heat is transferred from the hot coffee to the surroundings. Where does the energy come from? Since heat is a transfer of energy, if the surroundings gain energy the system must lose energy, $q_{\text{surr}} = -q$. However, since we assumed a capped container there is no change in volume and no work done, $w = 0$. Now consider a gas at high pressure confined in an insulated cylinder by an insulated piston, Figure 7.8.1b. When the stop is removed the system expands, doing work on the surroundings. Where does the energy come from? Since work is a transfer of energy, if the surroundings gain energy the system must

lose energy, $w_{\text{surr}} = -w$. However, since the process is adiabatic, assuming an insulated piston, the heat transferred must be zero, $q = 0$. In both cases the energy transfers come at the expense of the system. A hot container of coffee has the ability to transfer heat and a gas at high pressure has the ability to do work. The ability to do work in purely mechanical systems is called the potential energy. We can define a parallel concept for thermodynamic processes, the internal energy. The **internal energy** of a system is the ability of the system to transfer energy in the form of heat and work. But, what is the internal energy?

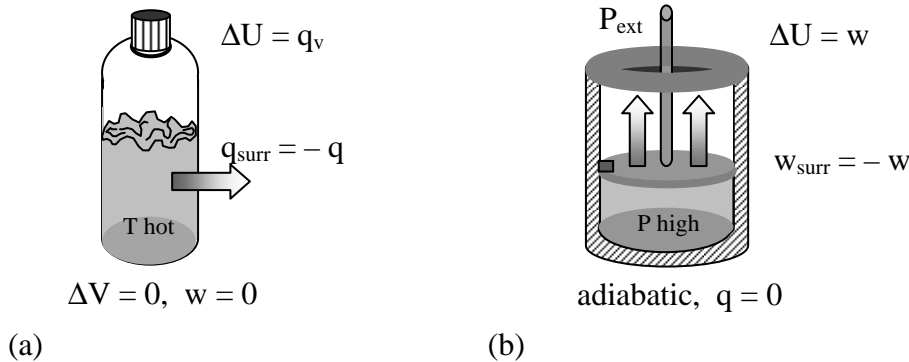


Figure 7.8.1: (a). A hot, closed, constant volume system with diathermal walls transfers heat to the surroundings with no work. (b). A high pressure, closed system with adiabatic walls does work on the surroundings with no heat transfer.

Consider another simple example. Assume you throw a battery across the room. The total energy of the battery is given by:

$$E = \frac{1}{2} mv^2 + mgh + U \quad 7.8.1$$

where m is the mass of the battery and the first term is the kinetic energy of the overall system, the second term is the gravitational potential energy, and the third is the internal energy of the system. The symbol U is used for the internal energy to differentiate it from the total energy of the system, E . The internal energy includes all the ways the system can have energy, except for the overall kinetic and gravitational energy of the system. The internal energy is sum of the average kinetic and potential energy of all of the atoms and molecules that make up the system. The internal energy includes the translational, rotational, vibrational, and electronic energy of the molecules plus any energy due to intermolecular forces. For the constant-volume hot coffee example, $\Delta U = q_v$, and for the adiabatic high pressure gas example, $\Delta U = w$. What happens in the general case when both heat and work transfers are possible?

The internal energy is given as the sum:

$$dU = dq + dw \quad 7.8.2$$

Eq. 7.8.2 is the mathematical statement of the **First Law** of thermodynamics. Heat and work are dependent on the path of the process. However, repeated experiments have shown that the sum of the heat and work transfers is independent of the path. The path independence of the internal energy is remarkable. A function that is independent of the path of the process is called a state function. Other examples of state functions include P , V , T , S , and density. The change in a state

function for a process is only a function of the initial and final states of the system, hence the name. The First Law can then also be stated as “internal energy is a state function.” Another common statement of the First Law based on Eq. 7.8.2 is that “the only way of changing the internal energy of system is through transfers of heat and work.” But, how can the sum of two path functions give a function that is independent of the path?

The heat transfer and work done by a given process are not independent; they both depend on the path of the process. For a given initial and final state, the First Law implies that for different paths the heat and work transfers compensate to give the same overall change. The consideration of cyclic processes is often a useful way to puzzle through thermodynamic relationships.

A **cyclic path** begins and ends with the same initial and final state. For any state function, the result of a cyclic process is no net change. In particular for the internal energy:

$$\oint dU = 0 \quad 7.8.3$$

The integral sign with the “o” indicates an integral over a cyclic path, Figure 7.8.2a. What might happen if internal energy weren't a state function? In proving a statement we often assume the converse and work through the ramifications until we come to an impossibility. Having reached an impossible condition we must conclude the original assumption was wrong. Assume that the internal energy is not a state function, which then implies that Eq. 7.8.3 does not hold. A cyclic process for a gas expansion and contraction in a closed system is diagrammed in Figure 7.8.2b, assuming U is not a state function.

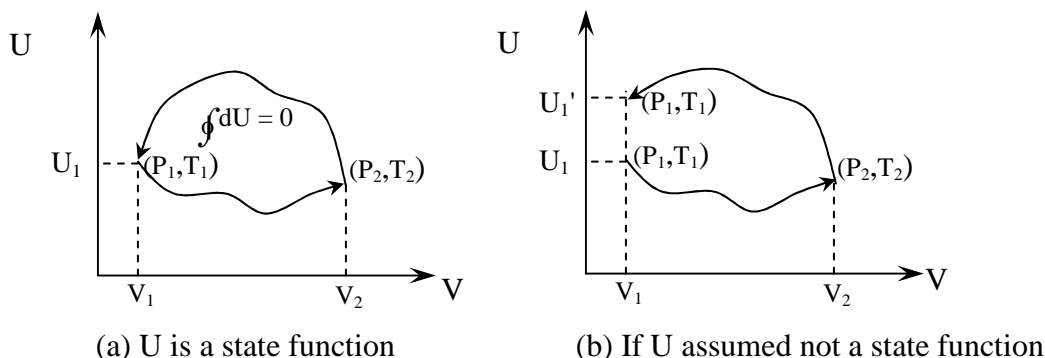


Figure 7.8.2: A cyclic process for a closed system. (a) The change in internal energy for a cyclic process is zero. (b) Assuming the converse leads to the possibility of perpetual motion. An increase in energy during the cyclic process might be able to do useful work with no other change in the system. U_1 is the initial internal energy and U_1' is the final internal energy.

If the integral for the cyclic process is not zero, the internal energy will be different upon completing the cycle. This difference in internal energy might then be available to do useful work. In other words, on taking the system from an initial state at P_1 , V_1 , and T_1 and returning the system to that same state, energy might be produced. The net result is the production of energy with no change in the system. Such a process has never been discovered and would constitute perpetual motion, which we know from experience to be impossible. Therefore, our original assumption that the internal energy is not a state function must be incorrect. Perpetual

motion that violates the First Law of thermodynamics is called perpetual motion of the **first kind**.

Internal Energy is Conserved: Eq. 7.8.2 also shows that internal energy is conserved. For example, for an isolated system, $\dot{d}q = 0$ and $\dot{d}w = 0$ giving $dU = 0$. So another statement of the First Law is that “the internal energy of an isolated system is constant.” Another way of noting the conservation of internal energy is to consider the interaction of a system with its surroundings. By the nature of heat and work as transfers of energy: $\dot{d}q_{\text{surr}} = -\dot{d}q$ and $\dot{d}w_{\text{surr}} = -\dot{d}w$, which necessarily gives $dU_{\text{surr}} = -dU$ by Eq. 7.8.2. The corresponding statement of the First Law then follows, “the internal energy change of the surroundings is equal in magnitude and opposite in sign to the internal energy change of the system.” The internal energy is a fundamental property of the system that keeps track of the energy changes for the system and the interrelationship of the system with its surroundings.

The Change in Internal Energy is the Heat Transfer at Constant Volume: How do we calculate changes in internal energy for simple processes? In general for a closed system with no non-PV work, we can substitute Eq. 7.4.3 into the definition of the internal energy in terms of heat and work transfers:

$$dU = \dot{d}q + \dot{d}w = \dot{d}q - P_{\text{ext}} dV \quad (\text{PV work only}) \quad 7.8.4$$

Note that “PV work only” implies a closed system, since the work of chemical change is a type of non-PV work. For constant volume processes $dV = 0$ and this equation reduces to:

$$dU = \dot{d}q_v \quad (\text{PV work only, cst. V}) \quad 7.8.5$$

This result is important. This result shows, assuming PV work only, that the:

heat transfer for a constant volume process is the internal energy change.

For changes in temperature at constant volume in a closed system, the heat transfer is given by Eq. 7.2.4 and substitution for the constant volume process into Eq. 7.8.5 gives a particularly simple result:

$$dU = C_v dT \quad (\text{PV work only, cst. V}) \quad 7.8.6$$

Or using the definition of the heat capacity from Eq. 7.2.5, substitution of Eq. 7.8.5 for $\dot{d}q_v$ gives:

$$\left(\frac{\partial U}{\partial T}\right)_v = C_v \quad (\text{closed, cst. V}) \quad 7.8.7$$

The convention is to use the “ \dot{d} ” symbol for path functions and the “ ∂ ” symbol for state functions in partial derivatives. Eqs. 7.8.6 and 7.8.7 integrate to:

$$\int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} C_v dT \quad (\text{closed, cst. V}) \quad 7.8.8$$

$$\Delta U = U_2 - U_1 = \int_{T_1}^{T_2} C_v dT \quad (\text{closed, cst. V}) \quad 7.8.9$$

If we assume a constant heat capacity over the temperature range, Eq. 7.8.9 gives:

$$\Delta U = C_v \Delta T \quad (\text{closed, cst. V \& } C_v) \quad 7.8.10$$

In other words, for a constant volume process in a closed system the internal energy is directly proportional to the temperature change.

The Change in Enthalpy is the Heat Transfer at Constant Pressure: We work at constant pressure more often than constant volume. What is the heat transfer for a constant pressure process? Consider a gas held at constant pressure in a cylinder by a piston, Figure 7.4.2a, with a change in volume from V_1 to V_2 . The gas is held at constant pressure by contact with the surroundings, $P = P_{\text{ext}}$. The internal energy change for the process is then given by Eq. 7.8.4 with $P = P_{\text{ext}}$:

$$\Delta U = U_2 - U_1 = q_p - P (V_2 - V_1) \quad (\text{PV work only, cst. P}) \quad 7.8.11$$

where q_p is the heat transfer at constant pressure. Solving for the heat transfer at constant pressure gives:

$$q_p = U_2 - U_1 + P (V_2 - V_1) \quad (\text{PV work only, cst. P}) \quad 7.8.12$$

We can rearrange this expression to group together the final and initial states:

$$q_p = (U_2 + P V_2) - (U_1 + P V_1) \quad (\text{PV work only, cst. P}) \quad 7.8.13$$

Since we often work at constant pressure, we suspect that this combination of terms will occur repeatedly. For convenience, we define a new thermodynamic function, the enthalpy, as:

$$H \equiv U + PV \quad 7.8.14$$

where P and V are for the system, not the surroundings. The enthalpy is a state function because U , P , and V are state functions. The enthalpy is also extensive, because U and V are extensive. For a general process with P , V , and T possibly all changing, the change in enthalpy from state 1 to state 2 is:

$$\Delta H = H_2 - H_1 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \quad 7.8.15$$

which is only a function of the two states of the system. The equation can be rearranged to find:

$$\Delta H = (U_2 - U_1) + (P_2 V_2 - P_1 V_1) = \Delta U + \Delta(PV) \quad 7.8.16$$

The enthalpy is particularly useful for constant pressure processes, where Eqs. 7.8.15 and 7.8.16 reduce to:

$$\Delta H = \Delta U + P \Delta V \quad (\text{cst. P}) \quad 7.8.17$$

Comparing Eqs. 7.8.13 and 7.8.17 we find that:

$$\Delta H = q_p \quad (\text{PV work only, cst. P}) \quad 7.8.18$$

This result is important. This result shows, assuming PV work only, that the:

heat transfer for a constant pressure process is the enthalpy change.

The internal energy and the enthalpy changes can be calculated for any process. However, at constant volume the internal energy has a simple meaning and at constant pressure the enthalpy has a simple meaning. For example, for a calorimeter that operates at constant volume, the heat

transfer gives the internal energy change directly, Eq. 7.8.5. For a calorimeter that operates at constant pressure, the heat transfer gives the enthalpy change directly, Eq. 7.8.18.

The differential form for infinitesimal changes in enthalpy from the definition $H \equiv U + PV$ is:

$$dH = dU + d(PV) \quad 7.8.19$$

The differential of the PV product can be taken using the product rule. For a general process:

$$dH = dU + PdV + VdP \quad 7.8.20$$

For a constant pressure process $dP = 0$, and this last result reduces to the differential form of Eq. 7.8.17:

$$dH = dU + PdV \quad (\text{cst. P}) \quad 7.8.21$$

In general $dU = \dot{d}q + \dot{d}w$. A constant pressure process with $P = P_{\text{ext}}$ gives $\dot{d}w = -P dV$. Substituting $dU = \dot{d}q - P dV$ into Eq. 7.8.21 gives:

$$dH = \dot{d}q + \dot{d}w + PdV = \dot{d}q_p + -P dV + PdV = \dot{d}q_p \quad (\text{cst. P}) \quad 7.8.22$$

which is a general proof in differential form of Eq. 7.8.18.

We can now use Eq. 7.8.22 to find the change in enthalpy for a change in temperature in a closed system. The heat transfer is given by Eq. 7.2.4 and substitution for the constant pressure process into Eq. 7.8.22, $dH = \dot{d}q_p$, gives a particularly simple result:

$$dH = C_p dT \quad (\text{PV work only, cst. P}) \quad 7.8.23$$

Or using the definition of the heat capacity from Eq. 7.2.5 gives:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p \quad (\text{closed, cst. P}) \quad 7.8.24$$

Eqs. 7.8.23 and 7.8.24 integrate to:

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p dT \quad (\text{PV work only, cst. P}) \quad 7.8.25$$

$$\Delta H = H_2 - H_1 = \int_{T_1}^{T_2} C_p dT \quad (\text{PV work only, cst. P}) \quad 7.8.26$$

If we assume a constant heat capacity over the temperature range, Eq. 7.8.25 gives:

$$\Delta H = C_p \Delta T \quad (\text{PV work only, cst. P \& C}_p) \quad 7.8.27$$

In other words, for a constant pressure process in a closed system the enthalpy change is directly proportional to the temperature change. We can use some other simple examples to help understand the meaning of enthalpy.

Consider the difference between the enthalpy and the internal energy for an ideal gas at constant pressure using Eq. 7.8.16. The change in volume can be calculated by noting that for n moles of an ideal gas in a closed system:

$$\Delta(PV) = nR \Delta T \quad (\text{ideal gas, closed}) \quad 7.8.28^\circ$$

Substituting this last result into Eq. 7.8.16 gives:

$$\Delta H = \Delta U + nR \Delta T \quad (\text{ideal gas, closed}) \quad 7.8.29^\circ$$

Example 7.8.1:

Calculate the change in internal energy and enthalpy for the constant pressure expansion of one mole of ideal gas as it is heated from 298.2 K to 398.2 K at 1.00 bar. Assume the gas is monatomic; monatomic gases have a constant pressure heat capacity of $C_p = \frac{5}{2} nR$.

Answer: The plan is to use Eq. 7.8.27 to find the enthalpy change, since the process is at constant pressure, and then use the definition of enthalpy to find the internal energy. We have two choices for the relationship between ΔU and ΔH , Eq. 7.8.17 or Eq. 7.8.29°. We will use both to verify that they give the same result. Using Eq. 7.8.27 for one mole of gas:

$$\begin{aligned}\Delta H &= C_p \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (1 \text{ mole})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(398.2 \text{ K} - 298.2 \text{ K}) \\ &= 2078.6 \text{ J} = 2.078 \text{ kJ}\end{aligned}$$

The initial and final volumes for the ideal gas are:

$$\begin{aligned}V_1 &= \frac{nRT_1}{P} = \frac{(1 \text{ mole})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(298.2 \text{ K})}{(1.00 \text{ bar})} = 24.79 \text{ L} = 2.479 \times 10^{-2} \text{ m}^3 \\ V_2 &= \frac{nRT_2}{P} = \frac{(1 \text{ mole})(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1})(398.2 \text{ K})}{(1.00 \text{ bar})} = 33.11 \text{ L} = 3.311 \times 10^{-2} \text{ m}^3 \\ \text{or } \Delta V &= (3.311 \times 10^{-2} \text{ m}^3 - 2.479 \times 10^{-2} \text{ m}^3) = 8.32 \times 10^{-3} \text{ m}^3.\end{aligned}$$

Rearranging Eq. 7.8.16 for this constant pressure process to find ΔU gives:

$$\begin{aligned}\Delta U &= \Delta H - P \Delta V = 2078.6 \text{ J} - (1.00 \text{ bar})(1 \times 10^5 \text{ Pa/1 bar})(8.32 \times 10^{-3} \text{ m}^3) \\ &= 2078.6 \text{ J} - 832 \text{ J} = 1247. \text{ J} = 1.25 \text{ kJ}\end{aligned}$$

Now, let's try working from Eq. 7.8.29°:

$$\begin{aligned}\Delta U &= \Delta H - nR \Delta T = 2078.6 \text{ J} + (1 \text{ mole})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(398.2 - 298.2 \text{ K}) \\ &= 2078.6 \text{ J} - 831.5 \text{ J} = 1247. \text{ J} = 1.25 \text{ kJ}\end{aligned}$$

Both equations give the same result. Now why is the internal energy change smaller than the enthalpy change for this expansion? Since the gas expands on heating, the gas does work, which lowers the internal energy: $\delta w = -P dV < 0$. However, $dH = dU + PdV$ for a constant pressure expansion and $PdV = -\delta w > 0$. So the enthalpy change is bigger than the internal energy change by the negative of the work of expansion.

How does the enthalpy change for processes that have a change in pressure? The enthalpy change for a reversible process is given by substituting Eq. 7.8.4 with $P = P_{\text{ext}}$ into Eqs. 7.8.20:

$$dH = \delta q - PdV + PdV + VdP = \delta q + VdP \quad (\text{reversible, PV work only}) \quad 7.8.30$$

For a reversible adiabatic process $\delta q = 0$ and the last equation simplifies to:

$$dH = VdP \quad (\text{reversible adiabatic or isolated, PV work only}) \quad 7.8.31$$

The last equation also holds for an isolated system since substitution of $\delta q = 0$ and $dV = 0$ into Eqs. 7.8.4 and 7.8.20 gives the same result. In other words, the enthalpy change can be

calculated for many different processes, but the enthalpy change is the heat transfer only for constant pressure processes. In addition, the next example shows that the enthalpy change with pressure is small for solids and liquids.

Example 7.8.2:

Calculate the change in enthalpy for 1.00 mol of water at 25°C for a change in pressure of 10.0 bar in a reversible adiabatic process.

Answer: One mole of water has a volume of $V_m = \mathcal{M}/d = 18.1 \text{ mL}$ at 25°C. Using Eq. 7.8.31, the change in volume is small for the pressure change, so to a good degree of approximation we can consider V a constant giving:

$$\Delta H = V\Delta P = 0.0181 \text{ L}(1 \text{ m}^3/1000 \text{ L})(10.0 \times 10^5 \text{ Pa}) = 18.1 \text{ J}$$

This change is negligible compared to the changes in enthalpy for typical phase transitions and chemical reactions. So the pressure dependence of the enthalpy for liquids and solids is often neglected.

Enthalpy is Not Conserved: Internal energy is conserved, but enthalpy is not conserved. Consider an isolated system as an example. For an isolated system internal energy is conserved, that is $\Delta U = 0$. However, Eq. 7.8.31 shows that the enthalpy change is non-zero if the pressure of the system changes. In addition, the enthalpy change for the surroundings is not necessarily equal in magnitude and opposite in sign to the enthalpy change for the system. So while both internal energy and enthalpy are state functions, only internal energy is conserved. This result underscores the fundamental importance of the internal energy.

Heat, work, internal energy, and enthalpy provide a careful accounting of the energy changes accompanying a process. This accounting is most useful and interesting for chemical purposes when we consider non-PV work. Sources of non-PV work will be critical as we consider chemical reactions, applications in biochemistry, and energy-related areas.

7.9 Systems Do Many Different Kinds of Work

The equation $dU = \delta q + \delta w$ is applicable to any kind of work. So far we have only explicitly considered the work of expansion, Eq. 7.8.3. The general form, $\delta w = F dx$, can be applied to other kinds of work as well, giving the change in internal energy as:

$$dU = \delta q - P_{\text{ext}}dV + F dx \tag{7.9.1}$$

Work against surface tension is an example. Consider a bubble with surface area σ , Figure 7.9.1a. For a given change in surface area the work is given by:

$$\delta w = \gamma d\sigma \tag{7.9.2}$$

where γ is the **surface tension**. Surface tension results from the imbalance of forces at an interface and therefore is a function of the properties of both of the phases that are in contact, Table 7.9.1. The units of the surface tension are J/m^2 or equivalently N/m .

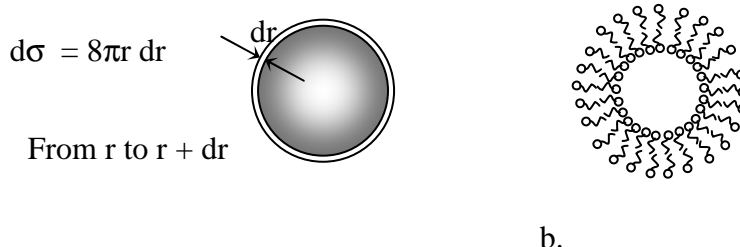


Figure 7.9.1: Surface tension arises from the imbalance of intermolecular forces when two phases come in contact. (a). When a bubble expands or contracts, work is done against the interfacial tension. (b). A phospholipid bilayer is another example of a system that can do interfacial work.

Table 7.9.1: Surface tension for several phases in contact.

Interface	γ (mN/m)
water/air	72.8
ethanol/air	22.3
hexane/air	18.4
hexane/water	51.1

The change in internal energy when PV and interfacial work are possible is then given by:

$$dU = \delta q - P_{\text{ext}}dV + \gamma d\sigma \quad 7.9.3$$

This formulation holds for any interfacial region, for example the surface of a rain drop. Free droplets of water are spherical to minimize their surface area, which lowers the internal energy with respect to interfacial work.

Another example is the work of **extension**, which is applicable to any elastic medium. Examples include springs, rubber bands, and muscles. The work of extension, Figure 7.9.2a, is given by

$$\delta w = f d\ell \quad 7.9.4$$

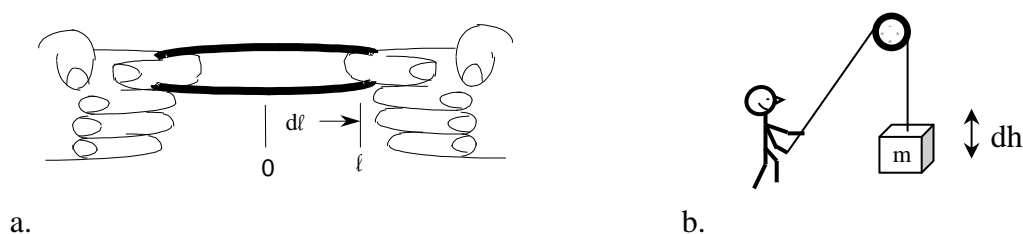


Figure 7.9.2: (a). The work of extension for an elastic body, $\delta w = f d\ell$. (b). Work against gravity, $\delta w = mg dh$.

Similarly work against gravity is given by the mass of the object, m , the acceleration due to gravity, g , and the change in height of the object, dh , Figure 7.9.2b:

$$dw = F dh = mg dh \quad 7.9.5$$

Another important form of non-PV work is electrical work. Consider a change in charge, dq_i , in a region with electric potential ϕ . The work done is given by:

$$dw = \phi dq_i \quad 7.9.6$$

The unit of charge is coulombs, C, and the unit of electric potential is volts, V, with $1 \text{ J} = 1 \text{ C V}$. The corresponding change in internal energy when expansion and electrical work are possible is then given by:

$$dU = \bar{d}q - P_{\text{ext}}dV + \phi dq_i \quad 7.9.7$$

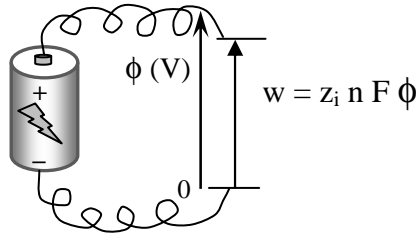


Figure 7.9.3: Electrical work is done when n moles of ions of charge z_i are moved into a region with electric potential ϕ . For Na^+ , $z_+ = +1$, and for Cl^- , $z_- = -1$. You can picture the electric potential difference as being established by a battery or other voltage source.

We often work with ionic species in solution. Consider n_i moles of ion type i . For ions with charge z_i the differential of the charge is given by:

$$dq_i = z_i e N_A dn_i \quad 7.9.8$$

where e is the elementary unit of charge, $(z_i e)$ is the charge on the ion in coulombs per ion, N_A is Avogadro's number, and dn_i is the change in number of moles of the ion. The total charge of one mole of elementary charges is given by the faraday:

$$1 F = e N_A = 1.602176 \times 10^{-19} \text{ C} (6.02214 \times 10^{23} \text{ mol}^{-1}) = 96485.3 \text{ C mol}^{-1} \quad 7.9.9$$

Substituting this identity into Eq. 7.9.8 gives:

$$dq_i = z_i F dn_i \quad 7.9.10$$

The electrical work done by placing a charge z_i on n_i moles of ions in a solution at constant electric potential ϕ is then given by the integral of Eq. 7.9.6:

$$w = \int_0^{z_i F n_i} \phi dq_i = \int_0^{n_i} z_i F \phi dn_i = z_i n_i F \phi \quad (\text{constant } \phi) \quad 7.9.11$$

The work of transferring Na^+ ions across the membrane of a neuron is a good example of electrical work. The work done by the transfer of n_i moles of ions between solutions at different electric potential is given by Eq. 7.9.6:

$$w = z_i n_i F \Delta\phi \quad 7.9.12$$

where $\Delta\phi$ is the difference in electric potential between the two solutions. A schematic diagram of a neuron and the corresponding plot of the electric potential is shown in Figure 7.9.4.

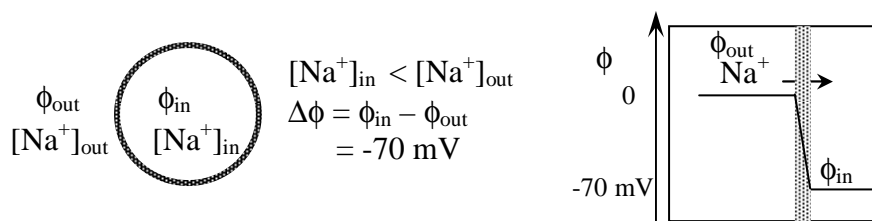
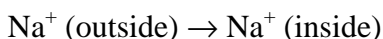


Figure 7.9.4: A neuron in its resting-state has a gradient of Na^+ , K^+ , and Ca^{2+} ions across the membrane, which results in an electric potential difference. The concentration of Na^+ outside the cell is greater than the concentration inside the cell.

The resting-state electric potential difference across a neuron is approximately -70 mV ; $\Delta\phi = \phi_{in} - \phi_{out} = -70 \text{ mV}$. A nerve impulse is caused by the rapid inrush or outrush of Na^+ , K^+ , and Ca^{2+} ions across the membrane, which depolarizes the membrane. The electrical work done in transferring a mole of Na^+ ions across the membrane is given by Eq. 7.9.13:



$$w_{\text{elec}} = (+1)(1 \text{ mol})(96485 \text{ C mol}^{-1})(-0.070 \text{ V}) = -6.75 \text{ kJ} \quad (\text{electrical work only}) \quad 7.9.13$$

The sign is negative because in this process the system does work, lowering the system's internal energy. Batteries are also good examples of electrical work.

Table 7.9.1. Non PV-work.

Type	work	change in internal energy
Surface tension	$\delta w = \gamma \delta\sigma$	$dU = \delta q - P_{\text{ext}}dV + \gamma \delta\sigma$
Extension	$\delta w = -f \delta l$	$dU = \delta q - P_{\text{ext}}dV - f \delta l$
Gravity	$\delta w = mg \delta h$	$dU = \delta q - P_{\text{ext}}dV + mg \delta h$
Electrical	$\delta w = \phi \delta q_i$ $\delta w = z_i F \phi \delta n_i$	$dU = \delta q - P_{\text{ext}}dV + \phi \delta q_i$ $dU = \delta q - P_{\text{ext}}dV + z_i F \phi \delta n_i$
Chemical	$\delta w = \mu_i \delta n_i$	$dU = \delta q - P_{\text{ext}}dV + \mu_i \delta n_i$

The most important type of work for chemists is the work of chemical change.⁹ Chemical synthesis is one particular example of chemical work. Chemical work can also be expressed in the general form of a force multiplied by a displacement, $\delta w = F dx$. For a single component i , the chemical work is expressed as:

$$\delta w = \mu_i dn_i \quad (\text{one component}) \quad 7.9.14$$

where the generalized force is called the **chemical potential**, μ_i , and the displacement is the change in number of moles of the component. A gradient in the chemical potential is the force for chemical change. We will have much more to say about chemical work. However, we need to discuss entropy and free energy before we can be more precise. The various work terms are summarized in Table 7.9.1.

7.10 Summary – Looking Ahead

The First Law of thermodynamics allows careful accounting of the energy changes in chemical systems. This accounting is possible because the internal energy of a system is conserved and a function only of the initial and final states of the system. The internal energy is a state function, while heat and work are dependent on the path of the process. The First Law determines the interrelationships of a system with its surroundings for exchanges of heat and work. The First Law is independent of the scale of macromolecular systems. The heat and work available account for chemical processes in the laboratory and in the environment. The concept of the conservation of internal energy is a useful tool for assessing processes within the laboratory, an ecosystem, or within a society. Organisms can be differentiated on the basis of their ability to use, produce, and process energy. Work comes in a variety of forms, including the work of chemical synthesis. As we consider progress in energy independence, decreased reliance on fossil fuels, and on ameliorating global climate change, one of the biggest needs is the development of advanced methods for energy storage. The production of liquid fuels and advanced batteries are examples of the storage of energy in chemical form.

The enthalpy is defined as a convenience to determine the heat transfer for processes at constant pressure. Enthalpy is an extensive state function, but enthalpy is not a conserved quantity. Therefore, enthalpy cannot replace internal energy as the primary tool for “balancing the books” on interconverting heat and work. One of the best ways to get used to a new state function is to do example problems. Our standard operating procedure when considering a new state function will be to consider homogeneous phases such as an ideal gas, then phase transitions, and then chemical reactions. In the next chapter we calculate the change in internal energy and enthalpy accompanying phase transitions and chemical reactions. The ultimate goal is to understand chemical transformations on a fundamental level so that we can design new chemical processes that meet our pressing needs.

7.11 Addendum: Partial Derivatives

Partial Derivatives Are Derivatives Taken One Variable at a Time: The ideal gas law is a convenient function to use to explore partial derivatives. The ideal gas law for a closed system defines a 3-dimensional surface. Consider P as the dependent variable with V and T the independent variables, Figure 7.11.1a. The independent variables are the ones that you control in the laboratory. The surface is the set of all P , V , and T values that satisfy the equation:

$$P = nRT/V$$

7.11.1

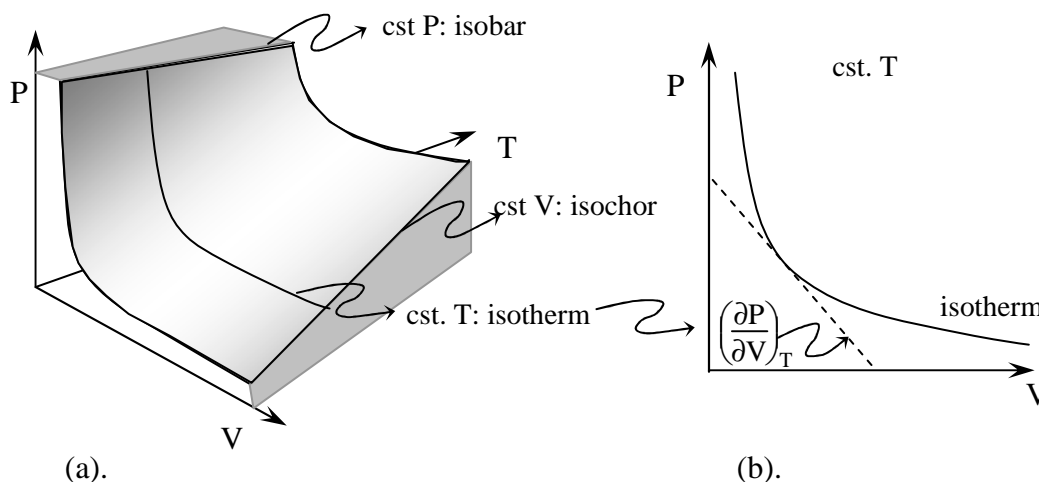


Figure 7.11.1: (a). P-V-T surface for an ideal gas. Partial derivatives are the slopes tangent to “slices” perpendicular to the axis for the constant variable.

An isotherm defines the P-V behavior in the plane that is perpendicular to the T axis, taken at the temperature of interest. One such slice is extracted to give Figure 7.11.1b. The slope of the P-V plot for this isotherm corresponds to the partial derivative:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} \quad 7.11.2$$

Let’s go through taking this partial derivative step-by-step. The quantities n and R are constants; n is constant because we assumed a closed system. In taking this partial derivative, we treat T as a constant also. In other words:

$$P = nRT/V = c/V \quad (\text{cst. } T) \quad 7.11.3$$

with $c = nRT$. And then:

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial(c/V)}{\partial V}\right)_T = -\frac{c}{V^2} \quad 7.11.4$$

Substituting $c = nRT$ back into this last equation gives Eq. 7.11.2. Partial derivatives are derivatives taken one variable at a time.

For practice consider the function:

$$f = m x^2 - 6 y \quad 7.11.5$$

As a first case, assume that m and y are both constant, with x the only variable. The normal one-dimensional derivative is then:

$$\frac{df}{dx} = \frac{d(m x^2 - 6 y)}{dx} = 2 m x \quad (\text{cst. } m, y) \quad 7.11.6$$

Now assume that only m is a constant, which gives two independent variables x and y . We can't take a one-dimensional derivative anymore, because both x and y can change. Instead, we can find the partial derivative with respect to x at constant y :

$$\left(\frac{\partial f}{\partial x}\right)_y = \left(\frac{\partial(m x^2 - 6 y)}{\partial x}\right)_y = 2 m x^2 \quad (\text{cst. } m) \quad 7.11.7$$

The result is just the same as when we assumed both m and y were constant. We can also find the partial derivative with respect to y :

$$\left(\frac{\partial f}{\partial y}\right)_x = \left(\frac{\partial(m x^2 - 6 y)}{\partial y}\right)_x = -6 \quad (\text{cst. } m) \quad 7.11.8$$

Partial derivatives are nothing extraordinary; we just keep everything constant except for the chosen independent variable. But, why are partial derivatives useful?

Total Differentials Express the Change in the Function with Each Independent Variable: First, we know that the volume of a closed system changes when we change the temperature and pressure. For a small change in temperature at constant pressure:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT \quad \text{compared to } y = m x \quad 7.11.9$$

which is just a linear equation for dV in terms of the variable dT and the slope $(\partial V/\partial T)_P$, Figure 7.11.2a.

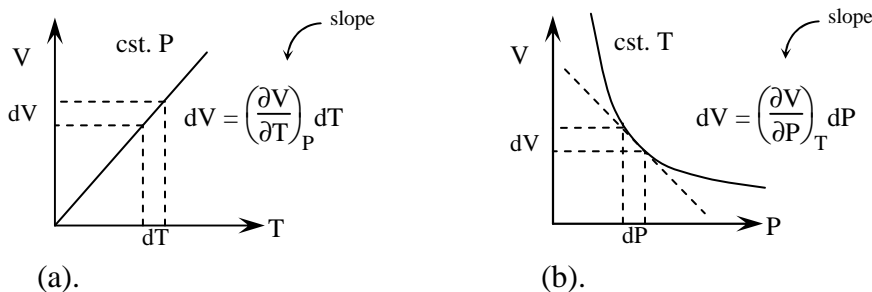


Figure 7.11.2: (a). The partial derivative $(\partial V/\partial T)_P$ is the slope of the function for small changes in temperature, at constant P . (b). The partial derivative $(\partial V/\partial P)_T$ is the slope of the function for small changes in pressure, at constant T .

On the other hand, for a small change in pressure at constant temperature:

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{compared to } y = m x \quad 7.11.10$$

which, again, is just a linear equation for dV in terms of the variable dP and the slope $(\partial V/\partial P)_T$, Figure 7.11.2b. Now what happens if both T and P change infinitesimally? The result is just the sum of Eq. 7.11.9 and 7.11.10:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad (\text{closed}) \quad 7.11.11$$

which is also Eq. 7.6.7. This last equation is called the **total differential**, since the equation gives the change in the dependent variable, V , with changes in all the independent variables. Notice that the total differential implies that the changes in dT and dP can be done in either order or at the same time; the result is the same, Figure 7.11.3. Notice this result is simply saying that the change in V is independent of the path. In other words, the total differential can be written for any state function, since state functions are path independent.

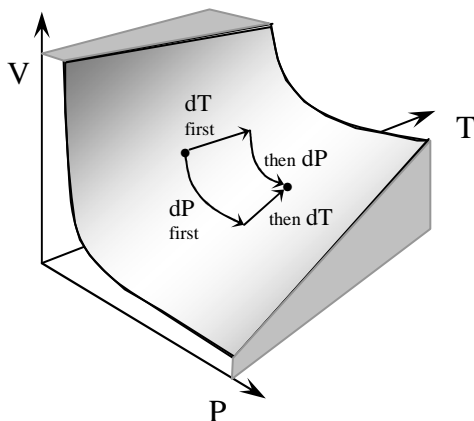


Figure 7.11.3: For the total differential, the changes in dT and dP can be taken in either order. Notice the change in axes from Figure 7.11.1.

The Total Differential can be Integrated Term-by-term: The path independence allows Eq. 7.11.11 to be integrated term-by-term:

$$\int_{V_1}^{V_2} dV = \int_{T_1}^{T_2} \left(\frac{\partial V}{\partial T}\right)_P dT + \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial P}\right)_T dP \quad 7.11.12$$

Even though your particular process may have a change in T and P simultaneously, we can think of the process as an equivalent two-step process; one at constant P and then one at constant T . The net result is the same, one-step or two in either order.

We can cast these ideas in general form. Given a function F of independent variables, x, y, z, \dots , we denote the independent variables by $F(x, y, z, \dots)$. If F is a state function, the differential of F is **exact**. An exact differential, dF , can be calculated only from the functional form of F without any additional information. On the other hand, the differential of a path function gives an inexact differential, which we denote with a dF . An inexact differential cannot be obtained by differentiation of a function of the state of the system alone. Exact differentials have useful properties. Given that F is a state function, dF is exact, and the total differential is given by:

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z,\dots} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z,\dots} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y,\dots} dz + \dots \quad (\text{exact}) \quad 7.11.13$$

with one term for each independent variable.

We used the general form of Eq. 7.11.13 to derive Eq. 7.6.7. Another example, which we will use in Chapter 9 is to consider the internal energy, for PV work only, as a function of temperature and volume, $U(T,V)$. The internal energy is a state function, the total differential of U is exact, and the total differential is given by:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad 7.11.14$$

Note that the first term on the right is just $C_v dT$. Similarly we can express the enthalpy as a function of P and T giving the exact total differential:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad 7.11.15$$

Note that the first term on the right is just $C_p dT$. Our major task for Chapter 9 is to show how and why these last two relationships are useful.

Partial Derivative Transformations: Partial derivatives can be manipulated just like the one-dimensional derivatives that we discussed in Addendum 1.5. For example, the *product rule* is analogous:

$$\left(\frac{\partial(PV)}{\partial P}\right)_T = P \left(\frac{\partial V}{\partial P}\right)_T + V \left(\frac{\partial P}{\partial P}\right)_T \quad \text{or} \quad \left(\frac{\partial(xy)}{\partial z}\right)_q = x \left(\frac{\partial y}{\partial z}\right)_q + y \left(\frac{\partial x}{\partial z}\right)_q \quad 7.11.16$$

Notice also that $(\partial P/\partial P)_T = 1$. The *inversion* relationship also works:

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T} \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad 7.11.17$$

The *chain rule* works the same way as for one-dimensional derivatives:

$$\left(\frac{\partial U}{\partial P}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V \quad \text{or} \quad \left(\frac{\partial y}{\partial x}\right)_q = \left(\frac{\partial y}{\partial z}\right)_q \left(\frac{\partial z}{\partial x}\right)_q \quad 7.11.18$$

Notice that in each of these relationships, Eq. 7.11.15-17, the same variable is held constant in each partial derivative.

Partial derivatives have two additional relationships that can be used to change the variable that is being held constant. We used the **Euler Chain Relationship** when we derived Eq. 7.6.14. To find $(\partial P/\partial T)_V$ we noted that the volume was held constant. We then set the total differential $dV = 0$ and solved:

$$dV = 0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{or} \quad dz = 0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad 7.11.19$$

Solving for $(\partial P/\partial T)_V$ or $(\partial x/\partial y)_z$ gives:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \quad 7.11.20$$

Using the *inversion* relationship, Eq. 7.11.17, we can also rewrite these last equations as:

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x \quad 7.11.21$$

These rearranged results look very similar to the normal chain rule, Eq. 7.11.18. However, note that the variable being held constant is different in each partial derivative and a minus sign is also present that is not present in the normal chain rule.

The remaining relationship also changes the variable that is held constant and the derivation of the relationship also starts with the total differential. Consider $U(T, V)$ or $F(x, y)$:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad \text{or} \quad dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy \quad 7.11.22$$

We can find relationships for partial derivatives such as $(\partial U/\partial T)_P$ or $(\partial F/\partial x)_z$ by dividing these last equations by dT at constant P , or dx at constant z , respectively:

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial F}{\partial x}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y \left(\frac{\partial x}{\partial x}\right)_z + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \quad 7.11.23$$

Notice that $(\partial T/\partial T)_P = 1$ and $(\partial x/\partial x)_z = 1$, which simplifies these particular expressions.

We would like to discourage you from memorizing these formulas. Rather, it is best to observe what each relationship does to the variables for the problem and then remember the process that was used. For example, for the *chain rule*, the same variable is held constant for each partial derivative. If you want to change the variable that is being held constant for a partial derivative, the transformations work through a total differential, as in Eq. 7.11.19 or 7.11.22. At this point, it will be best to do some examples to show the utility for these transformations. We will also present a general scheme for simplifying partial derivatives relationships in Chapter 9.

A Short-cut for Integrating Partial Derivative Relationships: Consider a process at constant P . The change in volume is given rigorously by Eq. 7.6.10 with $dP = 0$:

$$dV = V \alpha dT \quad 7.11.24$$

We sometimes use a mental short-cut that is easy to use and gives the same result. Rearrange Eq. 7.6.8 to give:

$$\left(\frac{\partial V}{\partial T}\right)_P = V \alpha \quad 7.11.25$$

We can think of “multiplying” Eq. 7.11.25 by dT on both sides to give:

$$\left(\frac{\partial V}{\partial T}\right)_P dT = V \alpha dT \quad \text{or} \quad dV = V \alpha dT \quad 7.11.26$$

where the ∂T and dT on the left effectively “cancel out.” The net result is the same as the rigorous Eq. 7.11.23. The issue is keeping proper track of the “ ∂ ” and “ d ” symbols. Even though our trick of multiplying both sides of the equation by dT is sloppy, the result is correct and easily derived.

Example 7.11.1:

Consider a constant volume process. (a). Integrate Eq. 7.11.14 rigorously to find the change in internal energy. (b). Use the “short-cut” method to find the same integral from Eq. 7.8.7.

Answer: (a). From Eq. 7.11.14 with $dV = 0$ and the substituting the definition of the constant volume heat capacity from Eq. 7.8.7 gives:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT = C_v dT \quad \text{or integrating} \quad \int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} C_v dT$$

(b). Starting from Eq. 7.8.7: $\left(\frac{\partial U}{\partial T}\right)_V = C_v$

Multiplying both sides of the last equation by dT gives:

$$\left(\frac{\partial U}{\partial T}\right)_V dT = C_v dT \quad \text{and “canceling” gives} \quad dU = C_v dT$$

as we derived in part (a), above.

In Chapter 9, we continue our development of the foundations of thermodynamics, which will include many examples of partial derivative transformations. If you have additional questions about differentials as you do the homework for this chapter, you might benefit from jumping ahead to Section 9.3, “*Differentials: A Differential is a Derivative Waiting to Happen,*” and Section 9.4, “*Integrating Differentials: A Differential is an Integral Waiting to Happen.*”

Chapter Summary

1. Thermodynamics is the study of the interconversion of heat and work.
2. Heat is the transfer of energy through random motions of molecules and work is the transfer of energy through organized motion. Thermal energy is random thermal kinetic energy.
3. Heat and work transfers are dependent on the path of the process.
4. The general types of processes are:

Constant pressure,	$\Delta P = 0:$	isobaric processes
Constant volume,	$\Delta V = 0:$	isochoric processes
Constant temperature,	$\Delta T = 0:$	isothermal processes
No heat transfer,	$q = 0:$	adiabatic processes

5. Diathermal barriers allow heat transfer and the attainment of thermal equilibrium. For adiabatic barriers no heat transfer is allowed.
6. Heat capacity is a path function. At constant volume the heat capacity and heat transfer are:

$$C_v \equiv \frac{dq_v}{dT} \quad dq_v = C_v dT \quad \text{and for a constant } C_v: q_v = C_v \Delta T$$

and at constant pressure:

$$C_p \equiv \frac{dq_p}{dT} \quad dq_p = C_p dT \quad \text{and for a constant } C_p: q_p = C_p \Delta T$$

7. The molar heat capacity or specific heat capacity are intensive properties of a substance:

$$C_{v,m} \equiv \frac{C_v}{n} \quad C_{p,m} \equiv \frac{C_p}{n} \quad C_{v,s} \equiv \frac{C_v}{w} \quad C_{p,s} \equiv \frac{C_p}{w}$$

8. Resistive electrical heating, or Joule heating, is used to calculate heat flow:

$$q = \int_0^t VI dt = \int_0^t I^2 R dt \quad \text{and for constant } V \text{ and } I: q = V I t = I^2 R t$$

9. Heat capacities are often approximated by a power series:

$$C_{p,m} = a + b T + c T^2 + d T^3 \quad \text{or} \quad C_{p,m} = A + B T + C T^2$$

10. Thermal conductivity can be expressed as a linear flux-force relationship:

$$J_q = -\mathcal{K} \frac{dT}{dx}$$

where \mathcal{K} is the thermal conductivity and dT/dx is the temperature gradient.

11. Radiative thermal energy transfer is given by the Stefan-Boltzmann law:

$$J_{q,\text{radiative}} = \sigma T^4 \quad \text{with } \sigma = 5.6704 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$$

12. The rate of thermal transfer, assuming a linear temperature gradient, is given by:

$$\frac{dq}{dt} = -\frac{\mathcal{K}\mathcal{A}}{\delta} (T - T_{\text{surr}})$$

assuming a linear temperature gradient over an interfacial area \mathcal{A} and thickness δ .

13. Thermal transfer changes the temperature of an object: $\frac{dq}{dt} = C_P \frac{dT}{dt}$

14. If the temperature of the surroundings is constant, Newton's Law of Cooling gives:

$$\frac{d(T - T_{\text{surr}})}{dt} = -\left(\frac{\mathcal{K}\mathcal{A}}{\delta C_P}\right) (T - T_{\text{surr}}) \quad \text{or} \quad (T - T_{\text{surr}}) = (T_o - T_{\text{surr}}) e^{-\frac{\mathcal{K}\mathcal{A}}{\delta C_P} t}$$

15. In differential scanning calorimetry, the heat flow difference between the sample and the reference is determined by:

$$\Delta \frac{dq_p}{dt} = \left(\frac{dq_p}{dt}\right)_{\text{sample}} - \left(\frac{dq_p}{dt}\right)_{\text{ref}}$$

The sample and reference are kept at the same temperature while the temperature of both is increased at a constant rate: $\alpha = dT/dt$.

16. In DSC the difference in the heat capacity of the sample and the reference is:

$$C_p(\text{sample}) - C_p(\text{ref}) = \Delta\left(\frac{dq_p}{dT}\right) = \left(\Delta\frac{dq_p}{dt}\right)\left(\frac{dt}{dT}\right)$$

17. The integral under the DSC peak, above the baseline, gives the total heat transferred and the enthalpy change for the process:

$$\int \frac{dq_{tr}}{dt} dt = q_{tr} = \Delta_{tr}H$$

18. For a general process, $dw = F dx$. Integration of the work is path dependent: $w = \int_{\text{path}} F dx$

19. Because heat and work are intrinsically energy transfers, the changes in energy for the system and surroundings are related by: $w_{\text{surr}} = -w$ and $q_{\text{surr}} = -q$

By convention, quantities without an explicit “surr” subscript are for the system.

20. The work of expansion, which is also called mechanical work or PV work, is a path function:

$$dw = -P_{\text{ext}} dV \quad \text{and} \quad w = -\int_{\text{path}} P_{\text{ext}} dV$$

21. For a constant external pressure, the expansion work is:

$$w = -\int_{V_1}^{V_2} P_{\text{ext}} dV = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \Delta V$$

22. For an isothermal reversible expansion, $P = P_{\text{ext}}$, and the work is the maximum amount of expansion work available for an isothermal process. For an ideal gas:

$$w = -\int_{V_1}^{V_2} nRT/V dV = -nRT \ln \frac{V_2}{V_1}$$

23. The Van der Waals equation of state, with Van der Waals coefficients a and b , is:

$$\left(P + a \frac{n^2}{V^2}\right) (V - nb) = nRT$$

The a -coefficient is a measure of the intermolecular attractions, and the b -coefficient is the excluded molar volume of the molecules.

24. The gas and liquid molar volumes for a substance approach the critical volume, V_c , as the system approaches the critical temperature, T_c , and pressure, P_c .
25. A gas above its critical temperature is called a super-critical fluid. Super-critical fluids have a smooth change in density as the volume is changed.
26. The Redlich-Kwong equation of state is valid over a wider range of gas densities than the Van der Waals equation of state. The A and B coefficients differ from the Van der Waals:

$$\left(P + A \frac{n^2}{T^{1/2}V(V+nB)}\right) (V - nB) = nRT$$

27. The compressibility factor is a measure of the deviation from ideal gas behavior:

$$z \equiv \frac{PV}{nRT} \quad \text{or} \quad PV = z nRT$$

28. The virial equation is a power series approximation for the compressibility factor:

$$z = \frac{PV}{nRT} = 1 + B(T) \left(\frac{n}{V}\right) + C(T) \left(\frac{n}{V}\right)^2 + D(T) \left(\frac{n}{V}\right)^3 + \dots$$

$B(T)$ and $C(T)$ are the second and third virial coefficients, respectively. The virial coefficients, are temperature dependent.

29. The Law of Corresponding States is that to a good approximation all gases follow the same equation of state when given as a function of the reduced variables:

$$P_R \equiv P/P_c \quad V_R \equiv V/V_c \quad T_R \equiv T/T_c$$

30. The total differential of the volume with respect to changes in temperature and pressure is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

31. The coefficient of thermal expansion and the isothermal compressibility are defined as, respectively:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

32. The total differential of the volume in terms of α and κ_T is: $dV = V \alpha dT - V \kappa_T dP$.

33. The values of α and κ_T are sufficient to completely specify the mechanical behavior of a system. The Euler chain relationship gives:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P}{\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T} = \frac{\alpha}{\kappa_T}$$

34. The differential $dV = V \alpha dT$ may be integrated with varying accuracy to give, for small changes: $V = V_o + V_o \alpha (T - T_o)$

$$\text{moderate changes: } V = V_o + V_o \alpha (T - T_o) + \frac{V_o \alpha^2}{2} (T - T_o)^2$$

$$\text{and large changes: } V = V_o e^{\alpha(T-T_o)}$$

35. The Zeroth Law of thermodynamics states: if systems A and B are at the same temperature and if systems B and C are at the same temperature then systems A and C will be at the same temperature. The Zeroth Law is the basis for establishing empirical temperature scales.

36. Temperature is the necessary variable for assessing if two systems are at thermal equilibrium. The relationship of the empirical temperature to P and V is established experimentally by the equation of state of the substance.

37. The internal energy is the sum of the kinetic energy and potential energy of all of the atoms and molecules that make up the system. The internal energy includes the translational, rotational, vibrational, and electronic energy of the molecules plus any energy due to intermolecular forces.

38. The First Law of thermodynamics is given by the definition: $dU = \delta q + \delta w$

39. Statements of the First Law include:

Internal energy is conserved.

Internal energy is a state function.

The only way of changing the internal energy of system is by transfers of heat and work.

$$\oint dU = 0$$

The internal energy of an isolated system is constant.

The internal energy change of the surroundings is equal in magnitude and opposite in sign to the internal energy change of the system.

40. For PV work only: $dU = \delta q - P_{\text{ext}} dV$ and for reversible processes: $dU = \delta q - P dV$.

41. The enthalpy is $H \equiv U + PV$. Enthalpy is an extensive state function, but is not conserved.

42. At constant volume for PV work only, $dU = \delta q_v$:

Heat transfer for a constant volume process is the internal energy change.

43. At constant pressure for PV work only, $dH = \delta q_p$:

Heat transfer for a constant pressure process is the enthalpy change.

44. At constant volume for a closed system for PV work only:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_v \quad dU = C_v dT \quad \text{and for a constant heat capacity:} \quad \Delta U = C_v \Delta T$$

45. At constant pressure for a closed system for PV work only:

$$\left(\frac{\partial H}{\partial T}\right)_P = C_p \quad dH = C_p dT \quad \text{and for a constant heat capacity:} \quad \Delta H = C_p \Delta T$$

46. For an ideal gas in a closed system: $d(PV) = nR dT$ or $\Delta(PV) = nR \Delta T$, giving:

$$dH = dU + nR dT \quad \text{or} \quad \Delta H = \Delta U + nR \Delta T$$

47. For a general process: $dH = dU + d(PV) = dU + PdV + VdP$

For a constant pressure process: $dH = dU + PdV$ or $\Delta H = \Delta U + P \Delta V$

For a reversible process for PV work only: $dH = \delta q + VdP$

For a reversible adiabatic process for PV work only: $dH = V dP$

For an isolated system: $dH = V dP$

48. The general form, $\delta w = F dx$, can be applied to many kinds of work giving (Table 7.9.1):

$$dU = \delta q - P_{\text{ext}}dV + F dx$$

49. Electrical work by a change in charge, dq_i , in a region with electric potential ϕ is $\delta w = \phi dq_i$.

The change in charge in coulombs for a change in moles of ion i is $dq_i = z_i F dn_i$, giving:

$$w = \int_0^{n_i} z_i F \phi dn_i = z_i n_i F \phi$$

50. The chemical work is $\delta w = \mu_i dn_i$ for a single component i , where the chemical potential, μ_i , is the force for chemical change.

51. An exact differential can be obtained by differentiation of a function of the state of the system, only. An inexact differential requires additional information concerning the path.

52. State functions have exact differentials. Path functions have inexact differentials.

53. The total differential for a state function, $F(x,y,z)$ is exact and is given as:

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z,\dots} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z,\dots} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y,\dots} dz$$

54. The Euler Chain Relationship for $(\partial x/\partial y)_z$ is obtained by setting $dz = 0$:

$$dz = 0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

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Problems: First Law of Thermodynamics

1. The movie "On Golden Pond" (IPC Films, 1982, 3 Academy Awards) was based on a play that was written about a summer home on Great Pond in central Maine. The surface area of Great Pond is $3.383 \times 10^7 \text{ m}^2$ and the volume is $2.130 \times 10^8 \text{ m}^3$. Great Pond is a large lake. The solar insolation for the Boston area is given in Chapter 2, Problem 13 as $4.16 \text{ kWh m}^{-2} \text{ day}^{-1}$. Calculate the total energy received by the lake per day on average and the corresponding change in temperature.
2. The specific heat capacity of stainless steel is $0.505 \text{ J K}^{-1} \text{ g}^{-1}$. A typical spoon weighs 20.9 g. Calculate the change in temperature when you place a spoon at $21.5 \text{ }^\circ\text{C}$ into 250. mL of hot coffee at $58.5 \text{ }^\circ\text{C}$. Assume the heat capacity of coffee is $4.179 \text{ J K}^{-1} \text{ g}^{-1}$ and the density is the density of water at $50 \text{ }^\circ\text{C}$ from Table 2.2.1.
3. Calculate the work done as a gas expands from an initial volume of 1.00 L to a final volume of 10.00 L against a constant external pressure of 1.000 atm.
4. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial volume of 1.00 L to a final volume of 10.00 L at 298.2 K. Compare the work done to the constant pressure expansion given in Problem 3.
5. Calculate the work done by one mole of an ideal gas in a reversible isothermal expansion from an initial pressure of 10.00 bar to a final pressure of 1.00 bar at 298.2 K. Compare the work done to the isothermal reversible expansion in Problem 4.

6. How ideal is water vapor? To answer this question, try the following problem: Assume a volume for a closed flask of 10.000 L, a temperature of 298.15K, and 0.01280 moles of water vapor. Calculate the pressure of water vapor in the flask using the ideal gas law and the Van der Waals equation of state and compare. (For comparison with the results of this problem, note that the vapor pressure of water at 298K is $P_{\text{vap}} = 23.8$ torr.)

7. Find the formula for the work done in the reversible isothermal expansion of a Van der Waals gas. (i.e. derive the equation corresponding to the ideal gas result: $w = -nRT \ln(V_2/V_1)$)

8. Derive the relationships between the second and third virial coefficients and the Van der Waals coefficients, as listed in Eqs. 7.5.6. Assume that the virial equation is truncated after the cubic term. [Hint: use the Taylor series approximation that for small x : $1/(1-x) \approx 1+x+x^2$]

9. Show that the Van der Waals equation is a cubic equation in the volume. In other words, rearrange the Van der Waals equation to give a cubic polynomial in V .

10. Use the virial equation to find the compressibility factor and the pressure for 10.00 mol of O_2 contained in a 1.000 L vessel at 298.15 K. Do attractive or repulsive forces dominate?

11. Integrate Eq. 7.6.9 for a small change in pressure during an isothermal process; that is, integrate $dV = -V \kappa_T dP$.

12. If the isothermal compressibility of acetone is $111 \times 10^{-6} \text{ atm}^{-1}$ at 14.2°C , what is the change in volume if the pressure is increased from 10.0 atm to 35.0 atm? Assume an initial volume of 1.00 L, the ΔP is small so that $V \approx V_0$, and the isothermal compressibility is constant.

13. From the definition of κ_T prove that for moderate changes in pressure:

$$V = V_0 - V_0 \kappa_T (P - P_0) + \frac{V_0 \kappa_T^2}{2} (P - P_0)^2.$$

14. Find the relationship between $\left(\frac{\partial T}{\partial P}\right)_V$ and α and κ_T . Use the Euler chain relationship.

15. Calculate the expansion work done by 1.00 L of water when the temperature is raised by 100.0°C . Assume the pressure is constant at 1.00 bar. This problem is an important issue when considering upwelling in the ocean.¹ The effect is small on the laboratory scale, but important on an oceanic scale.

16. The upwelling of deep-sea water is caused by large scale ocean currents such as the Atlantic current, which brings warm water north in the Atlantic. This current keeps western Europe warmer than other areas at similar latitude. As a packet of water rises, the pressure drops, the volume of the packet expands and the system does work.¹ The work is given by: $\delta w = PV\kappa_T dP$ at constant temperature. Derive this relationship.

17. The empirical temperature scale is based on the ideal gas thermometer. However, how can you build an ideal gas thermometer when there is no such thing as an ideal gas? The answer is that the effective temperature based on the ideal gas law is measured for differing amounts of gas and the results are extrapolated to zero gas density. The ideal gas thermometer can then be used

to calibrate more convenient thermometers. An ideal gas thermometer using helium is constructed with an internal volume for the gas of 0.500 L. The following table gives the number of moles of gas and the corresponding pressure at the fixed external temperature to be measured. Use the ideal gas law to calculate the effective temperature and then extrapolate the results to zero density.

n mol	0.040342	0.030256	0.020171	0.008068	0.004034
P (bar)	2.08225	1.56116	1.04042	0.41602	0.20797

18. The heat transfer at constant volume is the internal energy change and the heat transfer at constant pressure is the enthalpy change. Consider a constant volume process for an ideal gas. Even though the pressure isn't constant, you can still calculate ΔH . Calculate the change in enthalpy for a constant volume process given the temperature change, ΔT or dT . Assume a constant heat capacity over the temperature range. Give your answer in differential, derivative, and integrated (that is, ΔH) form.

19. Enthalpy is a state function. The heat transfer at constant pressure is the enthalpy change, $q_p = \Delta H$. Does this equality argue that q is a state function?

20. Determine if the following statements are true or false. If the statement is false, describe the changes that are necessary to make the statement true, if possible. If the statement is true but too restrictive, give the more general statement.²

- The work done by the system on the surroundings during a change in state is never greater than the decrease in the internal energy of the system.
- The enthalpy of a system cannot change during an adiabatic process.
- When a system undergoes a given isothermal change in state, the enthalpy change for the system does not depend upon the path of the process involved.
- When a change in state occurs, the increase in the enthalpy of the system must equal the decrease in the enthalpy of the surroundings.
- The equation $\Delta U = q + w$ is applicable to any macroscopic process, provided no electrical work is performed by the system on the surroundings.
- No change in state occurring in an isolated system can cause a change in the system's internal energy or enthalpy.
- For any constant pressure process, the increase in enthalpy equals the heat transferred whether or not electrical or chemical work is done during the process.
- A reversible process is one in which the internal energy lost by the system is just sufficient to restore the system to its original state.
- When a real gas expands into a vacuum, it does work because the molecules of the gas have been separated from one another against an attractive force.

21. The Gibbs free energy is usually considered a function of the temperature and the pressure, $G(T,P)$. Write the total differential of G with respect to changes in temperature and pressure.

22. Write the total differential of U considered as a function of T and P as independent variables.

23. (a). Integrate Eq. 7.6.10 for a constant temperature process using the total differential. Assume a narrow pressure range so that $V \approx V_0$ and κ_T is constant. (b). Integrate Eq. 7.6.9 using the “short-cut” method discussed in the Addendum, Sec. 7.11.

24. Find $(\partial P/\partial T)_V$ for a Van der Waals gas in a closed system.

25. The critical point is the point of inflection on the critical isotherm. The point of inflection corresponds to:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

Assume the gas is described by the Van der Waals equation of state. The two equations for the inflection point, above, provide two equations in two unknowns. Show that, in terms of the Van der Waals a and b coefficients, the critical volume, temperature, and pressure are given by:

$$V_c = 3nb \quad T_c = \frac{8a}{27bR} \quad P_c = \frac{a}{27b^2}$$

26. Calculate the change in internal energy for an adiabatic expansion of a gas for a change in volume from 1.00 L to 10.00 L against a constant external pressure of 1.00 bar.

27. Calculate the internal energy and enthalpy change for a constant volume process for one mole of ideal gas with a change in temperature from 298.2 K to 323.2 K. Assume the gas is diatomic with a constant volume heat capacity of $^{5/2} nR$. Explain the relative sizes of the internal energy and the enthalpy changes.

28. Find the enthalpy change for a constant volume process for a change in temperature ΔT of a Van der Waals gas, starting from the internal energy change, ΔU .

29. Heat capacities are often approximated by a power series: $C_{p,m} = a + b T + c T^2 + d T^3$. Find the change in molar enthalpy for a constant pressure process from T_1 to T_2 .

30. Consider the surroundings as a constant temperature and pressure reservoir. Show for a reversible adiabatic expansion of a gas from P_1 to P_2 that the enthalpy change of the system is not equal in magnitude and opposite in sign to the enthalpy change of the surroundings. In other words, enthalpy is not conserved.

31. Consider the surroundings as a constant temperature and pressure reservoir. Show for a constant pressure process that the enthalpy change of the system is equal in magnitude and opposite in sign to the enthalpy change of the surroundings.

Literature Cited:

1. T. J. McDougall, R. Feistel, “What causes the adiabatic lapse rate?” *Deep-Sea Research I*, **2003**, 50, 1523-1535.
2. J. Waser, K. N. Trueblood, C. M. Knobler, *Chem One, 2nd.Ed.*, McGraw Hill, New York, NY, 1980. pp. 414-415.