

Chapter 3: The First Law

Albert Einstein, a noted physicist, said of thermodynamics (Einstein, 1979)

“A law is more impressive the greater the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. (..) It is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown.”

Thermodynamics is the study of how energy flows into and out of systems and how it flows through the universe. People have been studying thermodynamics for a very long time and have developed the field a great deal, including the incorporation of high-level mathematics into the process. Many of the relationships may look cumbersome or complicated, but they are always describing the same basic thing: the flow of energy through the universe.

Energy, of course, can be used to do many useful things, such as allow us to drive our cars, use electronic devices, heat our homes, and cook our food. Chemistry is important as well since many of the processes in which we generate energy depend on chemical reactions (such as the combustion of hydrocarbons to generate heat or electron transfer reactions to generate electron flow.) The previous chapter investigated gases which are convenient systems to use to frame many discussions of thermodynamics since they can be modeled using specific equations of state such as the ideal gas law or the van der Waals law. These relationships depend on an important class of variables known as **state variables**.

State variables are those variables which depend only upon the current conditions affecting a system. Pressure, temperature and molar volume are examples of state variables. A number of variables required to describe the flow of energy in a system do depend on the pathway a system follows to come into its current state.

To illustrate the difference, consider climbing a mountain. You may choose to walk straight up the side of the mountain, or you may choose to circle the mountain several times in order to get to the top. These two pathways will differ in terms of how far you actually walk (a path-dependent variable) to attain the same change in altitude (an example of a state variable.)

Work and Heat

One of the pioneers in the field of modern thermodynamics was James P. Joule (1818 - 1889) (Encyclopedia.com, 2008). Among the experiments Joule carried out, was an attempt to measure the effect on the temperature of a sample of water that was caused by doing work on the water. Using a clever apparatus to perform work on water by using a falling weight to turn paddles

within an insulated canister filled with water, Joule was able to measure a temperature increase in the water.



Figure 1. James Prescott Joule (1818 - 1889)

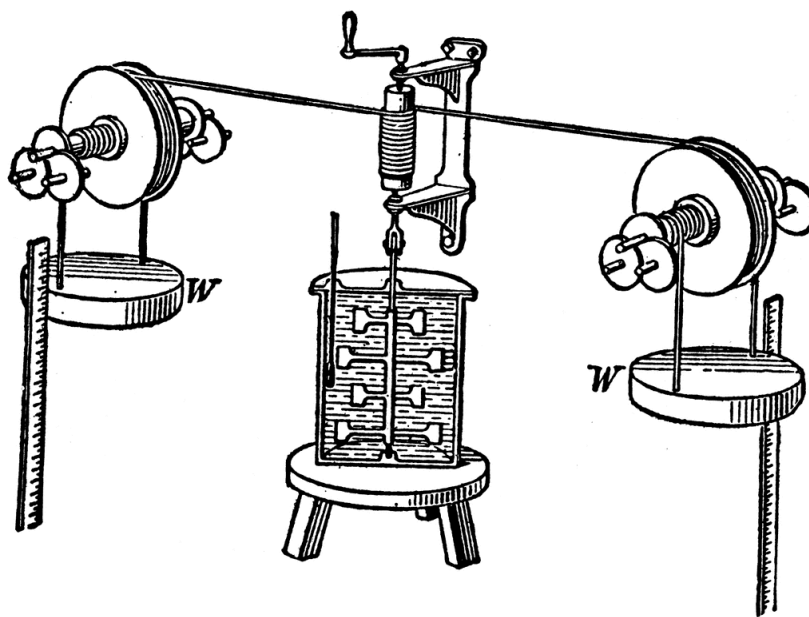


Figure 2. Joule's apparatus for measuring the work equivalent of heat.

Thus, Joule was able to show that work and heat can have the same effect on matter – a change in temperature! It would then be reasonable to conclude that heating, as well as doing work on a system will increase its energy content, and thus it's ability to perform work in the surroundings. This leads to an important construct of the **First Law of Thermodynamics**:

The capacity of a system to do work is increased by heating the system or doing work on it.

The **internal energy** (U) of a system is a measure of its capacity to supply energy that can do work within the surroundings, making U the ideal variable to keep track of the flow of heat and work energy into and out of a system. Changes in the internal energy of a system (ΔU) can be calculated by

$$\Delta U = U_f - U_i$$

where the subscripts i and f indicate initial and final states of the system. U as it turns out, is a state variable. In other words, the amount of energy available in a system to be supplied to the surroundings is independent on how that energy came to be available. That's important because the manner in which energy is transferred is path dependent.

There are two main methods energy can be transferred to or from a system. These are suggested in the previous statement of the first law of thermodynamics. Mathematically, we can restate the first law as

$$\Delta U = q + w \quad \text{or} \quad dU = dq + dw$$

where q is defined as the amount of energy that flows into a system in the form of **heat** and w is the amount of energy lost due to the system doing **work** on the surroundings.

Heat

Heat is the kind of energy that in the absence of other changes would have the effect of changing the temperature of the system. A process in which heat flows into a system is **endothermic** from the standpoint of the system ($q_{\text{system}} > 0$, $q_{\text{surroundings}} < 0$). Likewise, a process in which heat flows out of the system (into the surroundings) is called **exothermic** ($q_{\text{system}} < 0$, $q_{\text{surroundings}} > 0$). In the absence of any energy flow in the form of work, the flow of heat into or out of a system can be measured by a change in temperature. In cases where it is difficult to measure temperature changes of the system directly, the amount of heat energy transferred in a process can be measured using a change in temperature of the surroundings. (This concept will be used later in the discussion of calorimetry).

An infinitesimal amount of heat flow into or out of a system can be related to a change in temperature by

$$dq = C dT$$

where C is the **heat capacity** and has the definition

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

Heat capacities generally have units of ($\text{J mol}^{-1} \text{ K}^{-1}$) and magnitudes equal to the number of J needed to raise the temperature of 1 mol of substance by 1 K. Similar to a heat capacity is a **specific heat** which is defined per unit mass rather than per mol. The specific heat of water, for example, has a value of $4.184 \text{ J g}^{-1} \text{ K}^{-1}$ (at constant pressure – a pathway distinction that will be discussed later.)

Example:

How much energy is needed to raise the temperature of 5.0 g of water from 21.0 °C to 25.0 °C?

Solution:

$$q = mC\Delta T \qquad q = (5.0 \text{ g}) \left(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}} \right) (25.0^\circ\text{C} - 21.0^\circ\text{C}) \qquad q = 84 \text{ J}$$

What is a partial derivative?

A partial derivative, like a total derivative, is a slope. It gives a magnitude as to how quickly a function changes value when one of the dependent variables changes. Mathematically, a partial derivative is defined for a function $f(x_1, x_2, \dots, x_N)$ by

$$\left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} \equiv \lim_{\Delta x_i \rightarrow 0} \left(\frac{f(x_1, x_2, \dots, x_i + \Delta x_i, \dots, x_N) - f(x_1, x_2, \dots, x_i, \dots, x_N)}{\Delta x_i} \right)$$

Because it measures how much a function changes for a change in a given dependent variable, infinitesimal changes in the in the function can be described by

$$df = \sum_i \left(\frac{\partial f}{\partial x_i} \right)_{x_j \neq i} dx_i$$

So that each contribution to the total change in the function f can be considered separately.

For simplicity, consider an ideal gas. The pressure can be calculated for the gas using the ideal gas law. In this expression, pressure is a function of temperature and molar volume.

$$p(V, T) = \frac{RT}{V}$$

The partial derivatives of p can be expressed in terms of T and V as well.

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

And

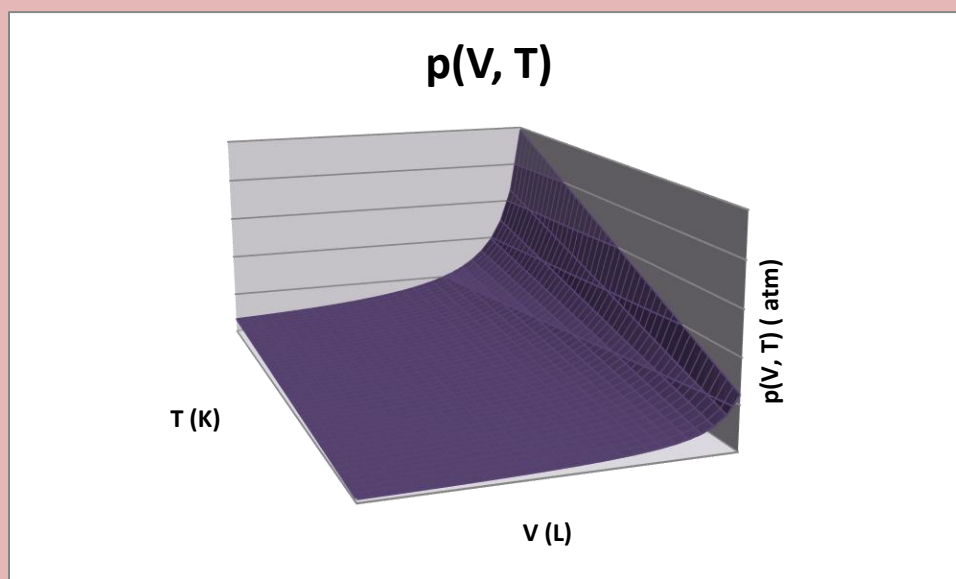
$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V}$$

So that the change in pressure can be expressed

$$dp = \left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT$$

Or

$$dp = \left(-\frac{RT}{V^2}\right) dV + \left(\frac{R}{V}\right) dT$$



Macroscopic changes can be expressed by integrating the individual pieces over appropriate intervals.

$$\Delta p = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial p}{\partial T}\right)_V dT$$

This can be thought of as two consecutive changes. The first is an isothermal expansion from V_1 to V_2 at T_1 and the second is an isochoric temperature change from T_1 to T_2 at V_2 . For example, suppose one needs to calculate the change in pressure for an ideal gas expanding from 1.0 L/mol at 200 K to 3.0 L/mol at 400 K. The set up might look as follows.

$$\Delta p = \int_{V_1}^{V_2} \left(-\frac{RT_1}{V^2} \right) dV + \int_{T_1}^{T_2} \left(\frac{R}{V_2} \right) dT$$

Or

$$\Delta p = \int_{1.0 \frac{L}{mol}}^{3.0 \frac{L}{mol}} \left(-\frac{R(200 K)}{V^2} \right) dV + \int_{200 K}^{400 K} \left(\frac{R}{\left(3.0 \frac{L}{mol} \right)} \right) dT$$

$$\Delta p = \left[\frac{R(200 K)}{V} \right]_{1.0 \frac{L}{mol}}^{3.0 \frac{L}{mol}} + \left[\frac{RT}{3.0 \frac{L}{mol}} \right]_{200 K}^{400 K}$$

$$\Delta p = R \left[\left(\frac{200 K}{3.0 L/mol} - \frac{200 K}{1.0 L/mol} \right) + \left(\frac{400 K}{3.0 L/mol} - \frac{200 K}{3.0 L/mol} \right) \right] = -5.47 \text{ atm}$$

Alternatively, one could calculate the change as an isochoric temperature change from T_1 to T_2 at V_1 followed by an isothermal expansion from V_1 to V_2 at T_2 :

$$\Delta p = \int_{T_1}^{T_2} \left(\frac{R}{V_1} \right) dT + \int_{V_1}^{V_2} \left(-\frac{RT_2}{V^2} \right) dV$$

Or

$$\Delta p = \int_{200 K}^{400 K} \left(\frac{R}{\left(1.0 \frac{L}{mol} \right)} \right) dT + \int_{1.0 \frac{L}{mol}}^{3.0 \frac{L}{mol}} \left(-\frac{R(400 K)}{V^2} \right) dV$$

$$\Delta p = \left[\frac{RT}{1.0 \frac{L}{mol}} \right]_{200 K}^{400 K} + \left[\frac{R(400 K)}{V} \right]_{1.0 \frac{L}{mol}}^{3.0 \frac{L}{mol}}$$

$$\Delta p = R \left[\left(\frac{400 K}{1.0 L/mol} - \frac{200 K}{1.0 L/mol} \right) + \left(\frac{400 K}{3.0 L/mol} - \frac{400 K}{1.0 L/mol} \right) \right] = -5.47 \text{ atm}$$

This results demonstrates an important property of pressure in that pressure is a state variable, and so the calculation of changes in pressure do not depend on the pathway!

Work

Work can take several forms, such as expansion against a resisting pressure, extending length against a resisting tension (like stretching a rubber band), stretching a surface against a surface tension (like stretching a balloon as it inflates) or pushing electrons through a circuit against a resistance.

The key to defining the work that flows in a process is to start with an infinitesimal amount of work defined by what is changing in the system.

Type of work	Displacement	Resistance	dw
Expansion	dV (volume)	$-p_{\text{ext}}$ (pressure)	$-p_{\text{ext}}dV$
Electrical	dQ (charge)	Ω (resistance)	$-\Omega dQ$
Extension	dL (length)	$-\tau$ (tension)	τdL
Stretching	dA	$-\sigma$ (surf. tens.)	σdA

The pattern followed is always an infinitesimal displacement multiplied by a resisting force. The total work can then be determined by integrating along the pathway the change follows.

Example:

What is the work done by 1.00 mol an ideal gas expanding from a volume of 22.4 L to a volume of 44.8 L against a constant external pressure of 0.500 atm?

Solution:

$$dw = -p_{\text{ext}}dV \quad w = -p_{\text{ext}} \int_{V_1}^{V_2} dV \quad w = -p_{\text{ext}}(V_2 - V_1)$$

$$w = -(0.500 \text{ atm})(44.8 \text{ L} - 22.4 \text{ L}) \left(\frac{8.314 \text{ J}}{0.08206 \text{ atm L}} \right)$$

$$= -1130 \text{ J} = -1.13 \text{ kJ}$$

Note: The ratio of gas law constants can be used to convert between atm·L and J quite conveniently!

Reversible and Irreversible Pathways

The most common example of work in the systems discussed in this book is the work of expansion. It is also convenient to use the work of expansion to exemplify the difference between work that is done reversibly and that which is done irreversibly. The example of expansion against a constant external pressure is an example of an irreversible pathway. It does not mean that the gas cannot be re-compressed. It does, however, mean that there is a definite direction of spontaneous change at all points along the expansion.

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Imagine instead a case where the expansion has no spontaneous direction of change as there is no net force push the gas to seek a larger or smaller volume. The only way this is possible is if the pressure of the expanding gas is the same as the external pressure resisting the expansion at all points along the expansion. With no net force pushing the change in one direction or the other, the change is said to be **reversible** or to occur **reversibly**. The work of a reversible expansion of an ideal gas is fairly easy to calculate.



If the gas expands reversibly, the external pressure (p_{ext}) can be replaced by a single value (p) which represents both the pressure of the gas and the external pressure.

$$dw = -p dV \quad \text{or} \quad w = - \int p dV$$

But now that the external pressure is not constant, p cannot be extracted from the integral. Fortunately, however, there is a simple relationship that tells us how p changes with changing V – the equation of state! If the gas is assumed to be an ideal gas

$$w = - \int p dV = - \int \left(\frac{nRT}{V} \right) dV$$

And if the temperature is held constant (so that the expansion follows an **isothermal** pathway) the nRT term can be extracted from the integral.

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Example:

What is the work done by 1.00 mol an ideal gas expanding reversibly from a volume of 22.4 L to a volume of 44.8 L at a constant temperature of 273 K?

Solution:

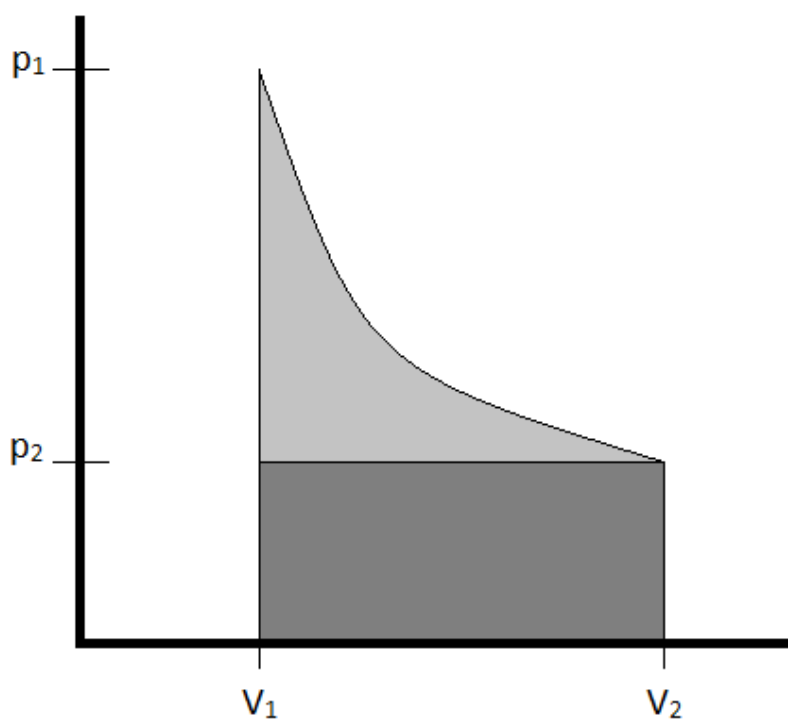
$$dw = -p dV \quad w = - \int_{V_1}^{V_2} p dV \quad w = - \int_{V_1}^{V_2} \left(\frac{nRT}{V} \right) dV \quad w = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$w = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{molK}} \right) (273 \text{ K}) \ln \left(\frac{44.8 \text{ L}}{22.4 \text{ L}} \right)$$

$$= -1570 \text{ J} = -1.57 \text{ kJ}$$

Note: A reversible expansion will always require more work than an irreversible expansion (such as an expansion against a constant external pressure) when the final states of the two expansions are the same!

The work of expansion can be depicted graphically as the area under the p-V curve depicting the expansion. For the previous two examples, for which the initial and final volumes were the same, and the constant external pressure of the irreversible expansion was the same as the final pressure of the reversible expansion, such a graph looks as follows.



The work is depicted as the shaded portion of the graph. It is clear to see that the reversible expansion (the work for which is shaded in both light and dark gray) exceeds that of the irreversible expansion (shaded in dark gray only) due to the changing pressure of the reversible expansion. In general, it will always be the case that the work generated by a reversible pathway connecting initial and final states will be the maximum work possible for the expansion.

It should be noted (although it will be proven in a later chapter) that ΔU for an isothermal reversible process involving only p-V work is 0 for an ideal gas. This is true because the internal energy, U , is a measure of a system's capacity to convert energy into work. In order to do this,

the system must somehow store that energy. The only mode in which an ideal gas can store this energy is in the translational kinetic energy of the molecules (otherwise, molecular collisions would not need to be elastic, which as you recall, was a postulate of the kinetic molecular theory!) And since the average kinetic energy is a function only of the temperature, it (and therefore U) can only change if there is a change in temperature. Hence, for any isothermal process for an ideal gas, $\Delta U = 0$. And, perhaps just as usefully, for an isothermal process involving an ideal gas, $q = -w$, as any energy that is expended by doing work must be replaced with heat, lest the system temperature drop.

Constant Volume Pathways

One common pathway which processes can follow is that of constant volume. This will happen if the volume of a sample is constrained by a great enough force that it simply cannot change. It is not uncommon to encounter such conditions with gases (since they are highly compressible anyhow) and also in geological formations, where the tremendous weight of a large mountain may force any processes occurring under it to happen at constant volume.

If reversible changes in which the only work that can be done is that of expansion (so-called p - V work) are considered, the following important result is obtained:

$$dU = dq + dw = dq - pdV$$

However, $dV = 0$ since the volume is constant! As such, dU can be expressed only in terms of the heat that flows into or out of the system at constant volume

$$dU = dq_v$$

Recall that dq can be found by

$$dq = \left(\frac{\partial q}{\partial T} \right) dT = C dT$$

This suggests an important definition for the **constant volume heat capacity** (C_v) which is

$$C_v \equiv \left(\frac{\partial U}{\partial T} \right)_v$$

Example:

Consider 1.00 mol of an ideal gas with $C_v = 3/2 R$ that undergoes a temperature change from 125 K to 255 K at a constant volume of 10.0 L. Calculate ΔU , q , and w for this change.

Solution:

$$w = 0 \text{ (due to constant volume)}$$

$$q = \int_{T_1}^{T_2} nC_V dT$$

Assuming C_V is independent of temperature:

$$q = nC_V \int_{T_1}^{T_2} dT$$

$$q = nC_V(T_2 - T_1)$$

$$q = (1.00 \text{ mol}) \left(\frac{3}{2} 8.314 \frac{\text{J}}{\text{mol K}} \right) (255 \text{ K} - 125 \text{ K}) = 1620 \text{ J} = 1.62 \text{ kJ}$$

$$\Delta U = q = 1.62 \text{ kJ}$$

Constant Pressure Pathways

Most laboratory-based chemistry occurs at constant pressure. Specifically, it is exposed to the constant air pressure of the laboratory, glove box, or other container in which reactions are taking place. For constant pressure changes, it is convenient to define a new thermodynamic quantity called **enthalpy**.

$$H \equiv U + pV \quad \text{or} \quad \begin{aligned} dH &\equiv dU + d(pV) \\ &= dU + pdV + Vdp \end{aligned}$$

For reversible changes at constant pressure ($dp = 0$) for which only p-V work is done

$$\begin{aligned} dH &= dq + dw + pdV + Vdp \\ &= dq - pdV + pdV + Vdp \\ &= dq \end{aligned}$$

And just as in the case of constant volume changes, this implies an important definition for the **constant pressure heat capacity**

$$C_p \equiv \left(\frac{\partial H}{\partial T} \right)_p$$

Example:

Consider 1.00 mol of an ideal gas with $C_p = 5/2 R$ that changes temperature change from 125 K to 255 K at a constant pressure of 10.0 atm. Calculate ΔU , ΔH , q , and w for this change.

Solution:

$$q = \int_{T_1}^{T_2} nC_p dT$$

Assuming C_p is independent of temperature:

$$q = nC_p \int_{T_1}^{T_2} dT$$

$$q = nC_p(T_2 - T_1)$$

$$q = (1.00 \text{ mol}) \left(\frac{5}{2} 8.314 \frac{\text{J}}{\text{mol K}} \right) (255 \text{ K} - 125 \text{ K}) = 2700 \text{ J} = 2.70 \text{ kJ}$$

$$\Delta H = q = 2.70 \text{ kJ}$$

$$\Delta U = \Delta H - \Delta(pV) \quad \Delta U = \Delta H - nR\Delta T$$

$$\Delta U = 2700 \text{ J} - (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (255 \text{ K} - 125 \text{ K}) = 1620 \text{ J} = 1.62 \text{ kJ}$$

$$w = \Delta U - q = 1.62 \text{ kJ} - 2.70 \text{ kJ} = -1.08 \text{ kJ}$$

Example:

Calculate q , w , ΔU , and ΔH for 1.00 mol of an ideal gas expanding reversibly and isothermally at 273 K from a volume of 22.4 L and a pressure of 1.00 atm to a volume of 44.8 L and a pressure of 0.500 atm.

Solution:

$$w = -nRT \ln \frac{V_2}{V_1} = -(1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (273 \text{ K}) \ln \left(\frac{44.8 \text{ L}}{22.4 \text{ L}} \right) = 1573 \text{ J} = 1.57 \text{ kJ}$$

$$\Delta U = q + w = q + 1.57 \text{ kJ} = 0 \quad q = -1.57 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta(pV) = 0 + 0 \quad (\Delta(pV) = 0 \text{ due to Boyle's Law!})$$

Adiabatic Pathways

An **adiabatic** pathway is defined as one in which no heat is transferred ($q = 0$). Under these circumstances, if an ideal gas expands, it is doing work ($w < 0$) against the surroundings (provided the external pressure is not zero!) and as such the internal energy must drop ($\Delta U < 0$). And since ΔU is negative, there must also be a decrease in the temperature ($\Delta T < 0$). How big

will the decrease in temperature be and on what will it depend? The key to answering these questions comes in the solution to how we calculate the work done.

If the adiabatic expansion is reversible and done on an ideal gas,

$$dw = -pdV \quad \text{and} \quad dw = nC_V dT$$

Equating these two terms yields

$$-pdV = nC_V dT$$

Using the ideal gas law for an expression for p ($p = nRT/V$)

$$-\frac{nRT}{V} dV = nC_V dT$$

And rearranging to gather the temperature terms on the right and volume terms on the left yields

$$\frac{dV}{V} = -\frac{C_V}{R} \frac{dT}{T}$$

This expression can be integrated on the left between V_1 and V_2 and on the right between T_1 and T_2 . Assuming that C_V/nR is independent of temperature over the range of integration, it can be pulled from the integrand in the term on the right.

$$\int_{V_1}^{V_2} \frac{dV}{V} = -\frac{C_V}{R} \int_{T_1}^{T_2} \frac{dT}{T}$$

The result is

$$\ln\left(\frac{V_2}{V_1}\right) = -\frac{C_V}{R} \ln\left(\frac{T_2}{T_1}\right) \quad \text{or} \quad \left(\frac{V_2}{V_1}\right) = \left(\frac{T_2}{T_1}\right)^{-\frac{C_V}{R}}$$

$$V_1 T_1^{\frac{C_V}{R}} = V_2 T_2^{\frac{C_V}{R}} \quad \text{or} \quad T_1 \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_V}} = T_2$$

Once ΔT is known, it is easy to calculate w , ΔU and ΔH .

Example:

1.00 mol of an ideal gas ($C_V = 3/2 R$) initially occupies 22.4 L at 273 K. The gas expands adiabatically and reversibly to a final volume of 44.8 L. Calculate ΔT , q , w , ΔU , and ΔH for the

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expansion.

Solution:

$$q = 0 \text{ (adiabatic)}$$

$$T_2 = (273 \text{ K}) \left(\frac{22.4 \text{ L}}{44.8 \text{ L}} \right)^{\frac{2}{3}} = 172 \text{ K} \quad \Delta T = (172 \text{ K} - 273 \text{ K}) = -101 \text{ K}$$

$$w = \Delta U = nC_V \Delta T = (1.00 \text{ mol}) \left(\frac{3}{2} 8.314 \frac{\text{J}}{\text{mol K}} \right) (-101 \text{ K}) = -1260 \text{ J}$$

$$\Delta H = \Delta U + nR\Delta T = -1260 \text{ J} + (1.00 \text{ mol}) \left(8.314 \frac{\text{J}}{\text{mol K}} \right) (-101 \text{ K}) = -2100 \text{ J}$$

The following table shows recipes for calculating q , w , ΔU , and ΔH for an ideal gas undergoing a reversible change along the specified pathway.

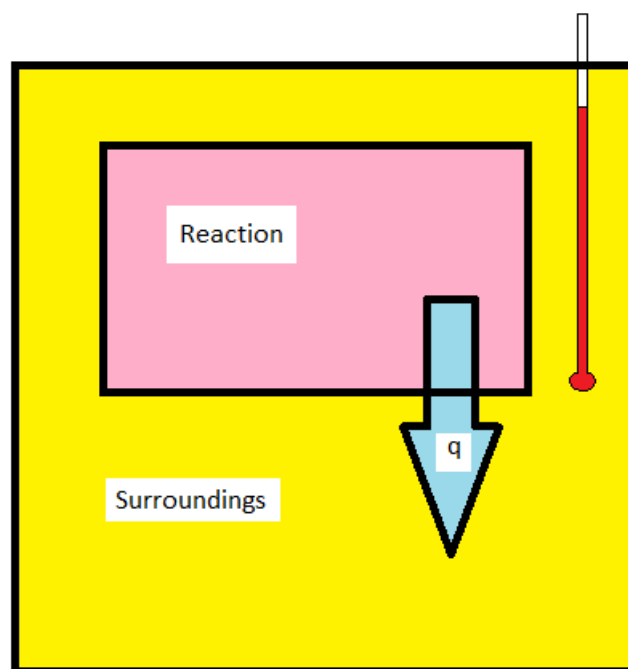
Pathway	q	w	ΔU	ΔH
Isothermal	$nRT \ln(V_2/V_1)$	$-nRT \ln(V_2/V_1)$	0	0
Isochoric	$C_V \Delta T$	0	$C_V \Delta T$	$C_V \Delta T + V\Delta p$
Isobaric	$C_p \Delta T$	$-p\Delta V$	$C_p \Delta T - p\Delta V$	$C_p \Delta T$
adiabatic	0	$C_V \Delta T$	$C_V \Delta T$	$C_p \Delta T$

Chemical Reactions

As chemists, we are concerned with chemical changes and reactions. The thermodynamics of chemical reactions can be very important in terms of controlling the production of desired products and preventing safety hazards such as explosions. As such, measuring and understanding the thermochemistry of chemical reactions is not only useful, but essential!

Calorimetry

The techniques of **calorimetry** can be used to measure q for a



chemical reaction directly. The enthalpy change for a chemical reaction is of significant interest to chemists. An exothermic reaction will release heat ($q_{\text{reaction}} < 0$, $q_{\text{surroundings}} > 0$) causing the temperature of the surrounding to increase. Conversely, an endothermic reaction ($q_{\text{reaction}} > 0$, $q_{\text{surroundings}} < 0$) will draw heat from the surroundings, causing the temperature of the surrounding to drop. Measuring the temperature change in the surroundings allows for the determination of how much heat was released or absorbed in the reaction.

Bomb Calorimetry

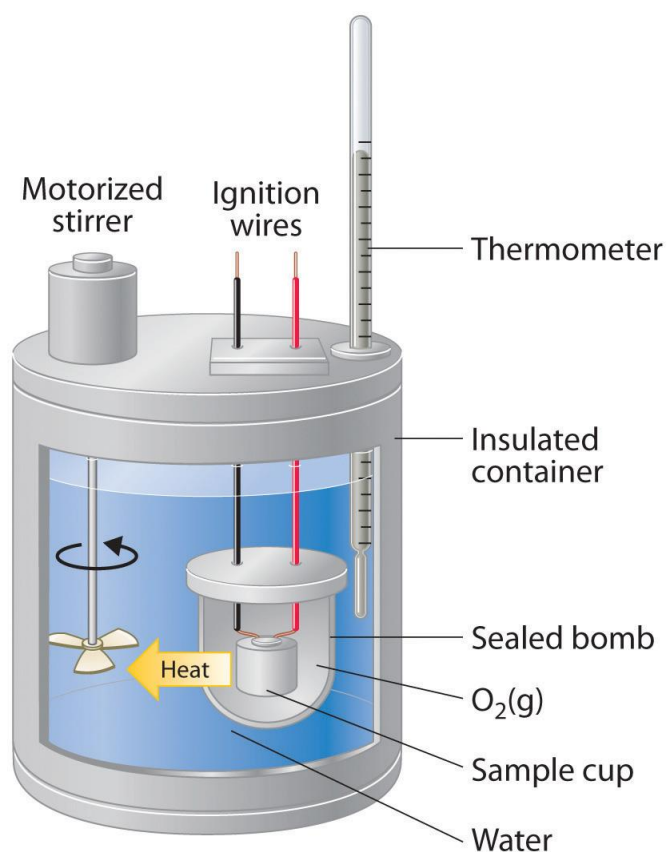
Bomb calorimetry is used predominantly to measure the heat evolved in combustion reactions, but can be used for a wide variety of reactions. A typical bomb calorimetry set up is shown here. The reaction is contained in a heavy metallic container (the bomb) forcing the reaction to occur at constant volume. As such, the heat evolved (or absorbed) by the reaction is equal to the change in internal energy (ΔU_{rxn}). The bomb is then submerged in a reproducible quantity of water, the temperature of which is monitored with a high-precision thermometer.

For combustion reactions, the bomb will be loaded with a small sample of the compound to be combusted, and then the bomb is filled with a high pressure (typically about 10 atm) of O_2 . The reaction is initiated by supplying heat using a short piece of resistive wire carrying an electrical current.

The calorimeter must be calibrated by carrying out a reaction for which ΔU_{rxn} is well known, so that the resulting temperature change can be related to the amount of heat released or absorbed. A commonly used reaction is the combustion of benzoic acid. This makes a good choice since benzoic acid reacts reliably and reproducibly under normal bomb calorimetry conditions. The “water equivalent” of the calorimeter can then be calculated from the temperature change using the following relationship:

$$W = \frac{n\Delta U_c + e_{\text{wire}} + e_{\text{other}}}{\Delta T}$$

where n is the number of moles of benzoic acid used, ΔU_c is the internal energy of combustion for benzoic acid (3225.7 kJ mol^{-1} at 25 °C), e_{wire} accounts for the energy released in the combustion of the



fuse wire, e_{other} account for any other corrections (such as heat released due to the combustion of residual nitrogen in the bomb), and ΔT is the measured temperature change in the surrounding water bath.

Once the “water equivalent” is determined for a calorimeter, the temperature change can be used to find ΔU_c for an unknown compound from the temperature change created upon combustion of a known quantity of the substance.

$$\Delta U_c = \frac{W\Delta T - e_{\text{wire}} - e_{\text{other}}}{n_{\text{sample}}}$$

The experiment above is known as “isothermal bomb calorimetry” as the entire assembly sits in a constant temperature laboratory. Another approach is to employ “adiabatic bomb calorimetry” in which the assembly sits inside of a water jacket, the temperature of which is controlled to match the temperature of the water inside the insulated container. By matching this temperature, there is no thermal gradient, and thus no heat leaks into or out of the assembly during an experiment (and hence the experiment is effectively “adiabatic.”

Finding ΔH_c

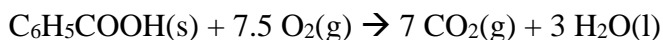
The **enthalpy of combustion** can be calculated from the internal energy change if the balanced chemical reaction is known. Recall from the definition of enthalpy

$$\Delta H = \Delta U + \Delta(pV)$$

and if the gas-phase reactants and products can be treated as ideal gases ($pV = nRT$)

$$\Delta H = \Delta U + RT\Delta n_{\text{gas}}$$

at constant temperature. For the combustion of benzoic acid at 25 °C



it can be seen that Δn_{gas} is -0.5 mol of gas for every mole of benzoic acid reacted.

Example:

A student burned a 0.7842 g sample of benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$) in a bomb calorimeter initially at 25.0 °C and saw a temperature increase of 2.02 °C. She then burned a 0.5348 g sample of naphthalene (C_{10}H_8) (again from an initial temperature of 25 °C) and saw a temperature increase of 2.24 °C. From this data, calculate ΔH_c for naphthalene (assuming e_{wire} and e_{other} are unimportant.)

Solution:

First, the water equivalent:

$$W = \frac{\left((0.7842 \text{ g}) \left(\frac{\text{mol}}{122.124 \text{ g}} \right) \right) \left(3225.7 \frac{\text{kJ}}{\text{mol}} \right)}{2.02 \text{ }^{\circ}\text{C}} = 10.254 \frac{\text{kJ}}{^{\circ}\text{C}}$$

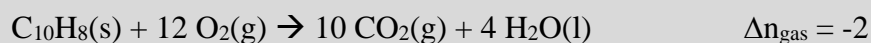
Then ΔU_c for the sample:

$$\Delta U_c = \frac{\left(10.254 \frac{\text{kJ}}{^{\circ}\text{C}} \right) (2.24 \text{ }^{\circ}\text{C})}{(0.5308 \text{ g}) \left(\frac{\text{mol}}{128.174 \text{ g}} \right)} = 5546.4 \frac{\text{kJ}}{\text{mol}}$$

ΔH_c is then given by

$$\Delta H_c = \Delta U_c + RT\Delta n_{\text{gas}}$$

The reaction for the combustion of naphthalene at 25 $^{\circ}\text{C}$ is:



So

$$\Delta H_c = 5546.4 \frac{\text{kJ}}{\text{mol}} + \left(8.314 \frac{\text{kJ}}{\text{mol K}} \right) (298 \text{ L})(-2) = 5541 \frac{\text{kJ}}{\text{mol}}$$

The literature value (Balcan, Arzik, & Altunata, 1996) is 5150.09 kJ/mol. So that's not too far off!

Temperature Dependence

It is often required to know thermodynamic functions (such as enthalpy) at temperatures other than those available from tabulated data. Fortunately, the conversion to other temperatures isn't difficult.

At constant pressure

$$dH = C_p dT$$

And so for a temperature change from T_1 to T_2

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

If C_p is independent of temperature,

$$\Delta H = C_p \Delta T$$

If the temperature dependence of the heat capacity is known, it can be incorporated into the integral. A common model used to fit heat capacities over broad temperature ranges is

$$C_p = a + bT + \frac{c}{T^2}$$

Since

$$\Delta H = \int_{T_1}^{T_2} C_p dT$$

the enthalpy change for the temperature change can be found by

$$\Delta H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) dT$$

Solving the definite integral yields

$$\begin{aligned} \Delta H &= \left[aT + \frac{bT^2}{2} - \frac{c}{T} \right]_{T_1}^{T_2} \\ &= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

This expression can then be used with experimentally determined values of a , b , and c , some of which are shown in the following table.

Substance	a (J mol ⁻¹ K ⁻¹)	b (J mol ⁻¹ K ⁻²)	c (J mol ⁻¹ K)
C(gr)	16.86	4.77×10^{-3}	-8.54×10^5
CO₂(g)	44.22	8.79×10^{-3}	-8.62×10^5
H₂O(l)	75.29	0	0
N₂(g)	28.58	3.77×10^{-3}	-5.0×10^4
Pb(s)	22.13	1.172×10^{-2}	9.6×10^4

Example:

What is the molar enthalpy change for a temperature increase from 273 K to 353 K for Pb(s)?

Solution:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad C_p(T) = a + bT + \frac{c}{T^2}$$

$$\Delta H = a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\begin{aligned} \Delta H &= 22.13 \frac{\text{J}}{\text{mol K}} (353 \text{ K} - 273 \text{ K}) \\ &+ \frac{1.172 \cdot 10^{-2}}{2} \frac{\text{J}}{\text{mol K}^2} [(353 \text{ K})^2 - (273 \text{ K})^2] \\ &- 9.6 \cdot 10^4 \frac{\text{J K}}{\text{mol}} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \end{aligned}$$

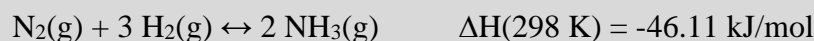
$$\begin{aligned} \Delta H &= 1770.4 \frac{\text{J}}{\text{mol}} + 293.5 \frac{\text{J}}{\text{mol}} + 470.5 \frac{\text{J}}{\text{mol}} \\ &= 2534.4 \frac{\text{J}}{\text{mol}} = 2.5 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

For chemical reactions, the reaction enthalpy at differing temperatures can be calculated from

$$\Delta H_{\text{rxn}}(T_2) = \Delta H_{\text{rxn}}(T_1) + \int_{T_1}^{T_2} \Delta C_p dT$$

Example:

The enthalpy of formation of NH₃(g) is -46.11 kJ/mol at 25 °C. Calculate the enthalpy of formation at 100 °C.

Solution:

Compound	C _p (J mol ⁻¹ K ⁻¹)
N ₂ (g)	29.12
H ₂ (g)	28.82
NH ₃ (g)	35.06

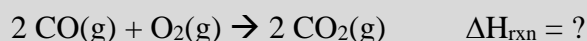
$$\begin{aligned}
 \Delta H(373\text{ K}) &= \Delta H(298\text{ K}) + \Delta C_p \Delta T \\
 &= -46110 \frac{\text{J}}{\text{mol}} + \left(2(35.06 \frac{\text{J}}{\text{molK}}) - (29.12 \frac{\text{J}}{\text{molK}}) - 3(28.82 \frac{\text{J}}{\text{molK}}) \right) (373\text{ K} - 298\text{ K}) \\
 &= -4951.5 \frac{\text{J}}{\text{mol}} = -49.5 \frac{\text{kJ}}{\text{mol}}
 \end{aligned}$$

Reaction Enthalpies

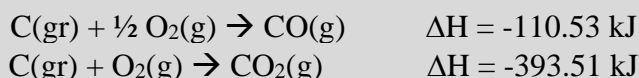
Reaction enthalpies are important, but difficult to tabulate. However, because enthalpy is a state function, it is possible to use **Hess' Law** to simplify the tabulation of reaction enthalpies. Hess' Law is based on the addition of reactions. By knowing the reaction enthalpy for constituent reactions, the enthalpy of a reaction that can be expressed as the sum of the constituent reactions can be calculated. The key lies in the canceling of reactants and products that occur in the “data” reactions but not in the “target reaction.”

Example:

Find ΔH_{rxn} for the reaction

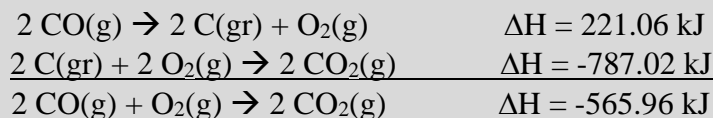


Given



Solution:

The target reaction can be generated from the data reactions.



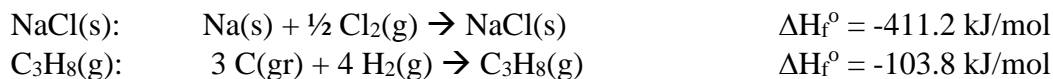
Standard Enthalpy of Formation

One of the difficulties with many thermodynamic state variables (such as enthalpy) is that while it is possible to measure changes, it is impossible to measure an absolute value of the variable itself. In these cases, it is necessary to define a zero to the scale defining the variable. For enthalpy, the definition of a zero is that the standard enthalpy of formation of a pure element in its standard state is zero. All other enthalpy changes are defined relative to this standard.

Thus it is essential to very carefully define a standard state.

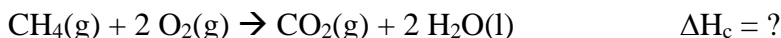
Definition: *The standard state of a substance is the most stable form of that substance at 1 atmosphere pressure and the specified temperature.*

Using this definition, a convenient reaction for which enthalpies can be measured and tabulated is the **standard formation reaction**. This is a reaction which forms one mole of the substance of interest in its standard state from elements in their standard states. The enthalpy of a standard formation reaction is the **standard enthalpy of formation** (ΔH_f°). Some examples are



It is important to note that the standard state of a substance is temperature dependent. For example, the standard state of water at -10°C is solid, whereas the standard state at room temperature is liquid.

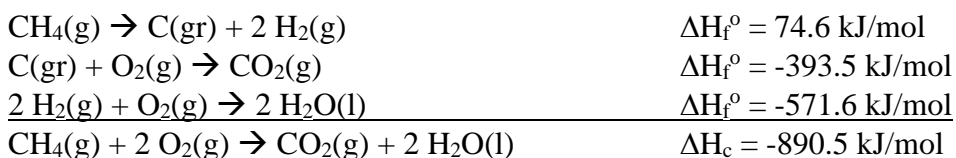
Once these values are tabulated, calculating reaction enthalpies becomes a snap. Consider the combustion of methane (at 25°C) as an example.



The reaction can be expressed as a sum of a combination of the following standard formation reactions.



The target reaction can be generated from the following combination of reactions



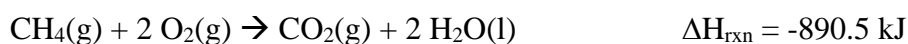
Alternately, the reaction enthalpy could be calculated from the following relationship

$$\Delta H_{\text{rxn}} = \sum_{\text{products}} \nu \cdot \Delta H_f^\circ - \sum_{\text{reactants}} \nu \cdot \Delta H_f^\circ$$

where ν is the stoichiometric coefficient of a species in the balanced chemical reaction. For the combustion of methane, this calculation is

$$\begin{aligned}
 \Delta H_{\text{rxn}} &= (1 \text{ mol})(\Delta H_f^\circ(\text{CO}_2)) + (2 \text{ mol})(\Delta H_f^\circ(\text{H}_2\text{O})) - (1 \text{ mol})(\Delta H_f^\circ(\text{CH}_4)) \\
 &= (1 \text{ mol})(-393.5 \frac{\text{kJ}}{\text{mol}}) + (2 \text{ mol})(-285.8 \frac{\text{kJ}}{\text{mol}}) - (1 \text{ mol})(-74.6 \frac{\text{kJ}}{\text{mol}}) \\
 &= -890.5 \text{ kJ}
 \end{aligned}$$

A note about units is in order. Note that reaction enthalpies have units of kJ, whereas enthalpies of formation have units of kJ/mol. The reason for the difference is that enthalpies of formation (or for that matter enthalpies of combustion, sublimation, vaporization, fusion, etc.) refer to specific substances and/or specific processes involving those substances. As such, the total enthalpy change is scaled by the amount of substance used. General reactions, on the other hand, have to be interpreted in a very specific way. When examining a reaction like the combustion of methane



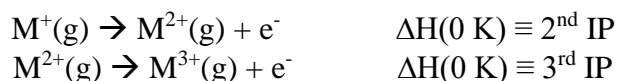
the correct interpretation is that the reaction of one mole of $\text{CH}_4(\text{g})$ with two moles of $\text{O}_2(\text{g})$ to form one mole of $\text{CO}_2(\text{g})$ and two moles of $\text{H}_2\text{O}(\text{l})$ releases 890.5 kJ at 25 °C.

Ionization Reactions

Ionized species appear throughout chemistry. The energy changes involved in the formation of ions can be measured and tabulated for several substances. In the case of the formation of positive ions, the enthalpy change to remove a single electron at 0 K is defined as the **ionization potential**.



The removal of subsequent electrons requires energies called the 2nd Ionization potential, 3rd ionization potential, and so on.



An atom can have as many ionization potentials as it has electrons, although since very highly charged ions are rare, only the first few are important for most atoms.

Similarly, the **electron affinity** can be defined for the formation of negative ions. In this case, the first electron affinity is defined by



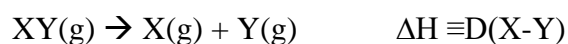
The minus sign is included in the definition in order to make electron affinities mostly positive. Some atoms (such as noble gases) will have negative electron affinities since the formation of a

negative ion is very unfavorable for these species. Just as in the case of ionization potentials, an atom can have several electron affinities.



Average Bond Enthalpies

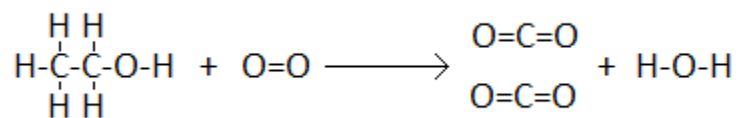
In the absence of standard formation enthalpies, reaction enthalpies can be estimated using average bond enthalpies. This method is not perfect, but it can be used to get ball-park estimates when more detailed data is not available. A **bond dissociation energy** is defined by



In this process, one adds energy to the reaction to break bonds, and extracts energy for the bonds that are formed.

$$\Delta H_{\text{rxn}} = \sum(\text{bonds broken}) - \sum(\text{bonds formed})$$

As an example, consider the combustion of ethanol:



In this reaction, five C-H bonds, one C-C bond, and one C-O bond, and one O=O bond must be broken. Also, four C=O bonds, and one O-H bond are formed.

Bond	Average Bond Energy (kJ/mol)
C-H	413
C-C	348
C-O	358
O=O	495
C=O	799
O-H	463

The reaction enthalpy is then given by

$$\begin{aligned} \Delta H_{\text{c}} = & 5(413 \text{ kJ/mol}) + 1(348 \text{ kJ/mol}) + 1(358 \text{ kJ/mol}) + 1(495 \text{ kJ/mol}) \\ & - 4(799 \text{ kJ/mol}) - 2(463 \text{ kJ/mol}) \end{aligned}$$

$$\Delta H_c = -856 \text{ kJ/mol}$$

Because the bond energies are defined for gas-phase reactants and products, this method does not account for the enthalpy change of condensation to form liquids or solids, and so the result may be off systematically due to these differences. Also, since the bond enthalpies are averaged over a large number of molecules containing the particular type of bond, the results may deviate due to the variance in the actual bond enthalpy in the specific molecule under consideration. Typically, reaction enthalpies derived by this method are only reliable to within $\pm 5\text{-}10\%$.

Lattice Energy

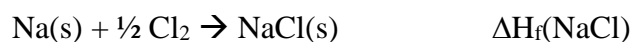
An important enthalpy change is the **lattice energy**. This is the energy necessary to take one mole of a crystalline solid to ions in the gas phase. For NaCl(s), the lattice energy is defined as the enthalpy of the reaction



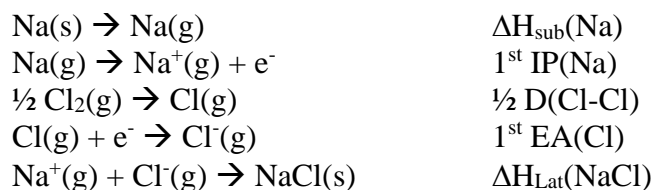
The Born-Haber Cycle

A very handy construct in thermodynamics is that of the thermodynamic cycle. This can be represented graphically to help to visualize how all of the pieces of the cycle add together. A very good example of this is the **Born-Haber cycle**, describing the formation of an ionic solid.

Two pathways can be envisioned for the formation. Added together, the two pathways form a cycle. In one pathway, the ionic solid is formed directly from elements in their standard states.



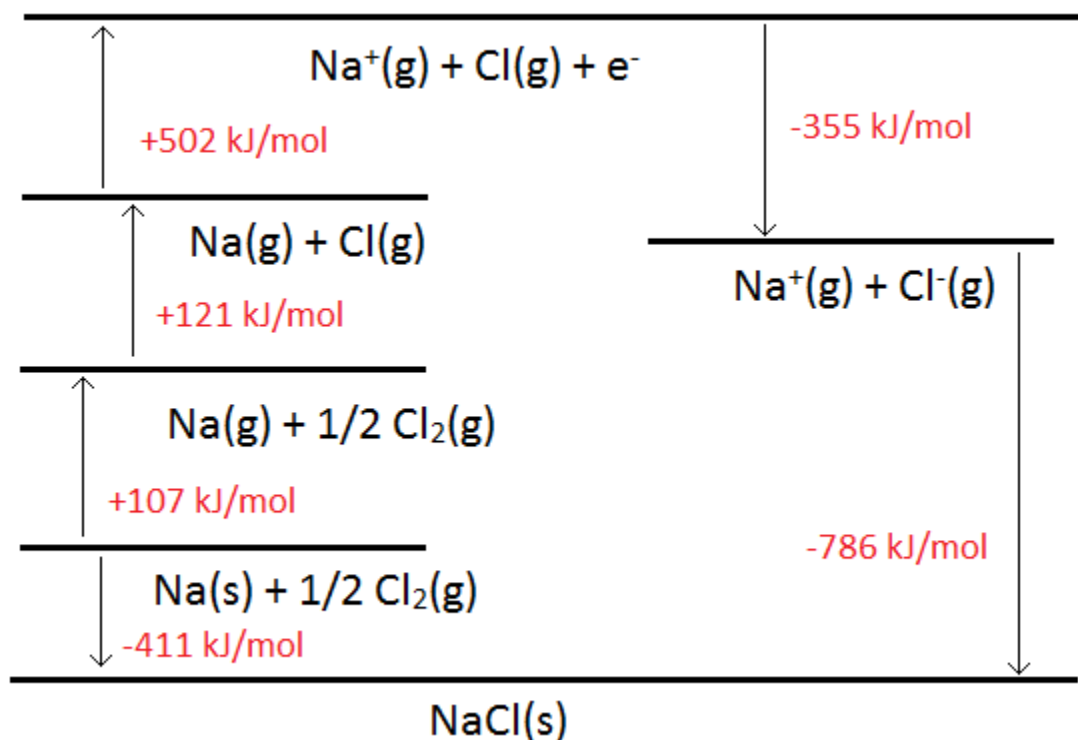
The other pathway involves a series of steps that take the elements from neutral species in their standard states to ions in the gas phase.



It should be clear that when added (after proper manipulation if needed), the second set of reactions yield the first reaction. Because of this, the total enthalpy changes must all add.

$$\Delta H_{\text{sub}}(\text{Na}) + 1^{\text{st}} \text{ IP}(\text{Na}) + \frac{1}{2} D(\text{Cl-Cl}) + 1^{\text{st}} \text{ EA}(\text{Cl}) + \Delta H_{\text{Lat}}(\text{NaCl}) = \Delta H_f(\text{NaCl})$$

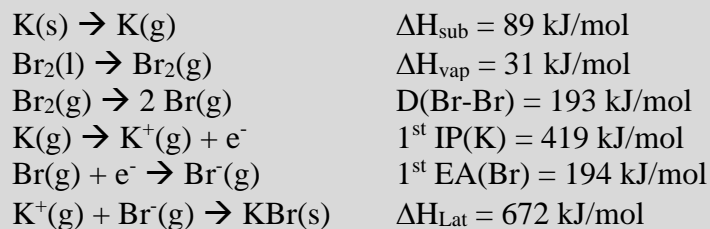
This can be depicted graphically, the advantage being that arrows can be used to indicate endothermic or exothermic changes. An example of the Born-Haber Cycle for NaCl is shown below.



In many applications, all but one leg of the cycle is known, and the job is to determine the magnitude of the missing leg.

Example:

Given the following data, find ΔH_f for KBr.



Answer:

$$\Delta H_f = -246 \text{ kJ/mol}$$

Note: This cycle required the extra leg of the vaporization of Br₂. Many cycles involve ions with greater than unit charge and may require extra ionization steps as well!

References

- Balcan, M., Arzik, S., & Altunata, T. (1996). The determination of the heats of combustion and the resonance energies of some substituted naphthalenes. *Thermichimica Acta*, 278, 49-56.
- Einstein, A. (1979). *Autobiographical Notes. A Centennial Edition*. Open Court Publishing Company.
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Vocabulary and Concepts

adiabatic	60	heat capacity.....	51
Bomb calorimetry	63	Hess' Law	68
bond dissociation energy.....	71	internal energy	51
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endothermic.....	51	specific heat	52
enthalpy	59	standard enthalpy of formation	69
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Learning Objectives

After mastering the material covered in this chapter, one will be able to:

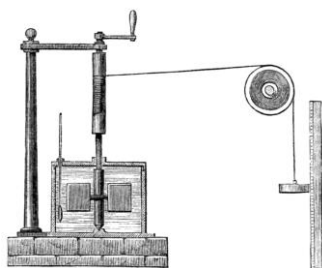
1. Define the internal energy of a system as a measure of its capacity to do work on its surroundings.
2. Define work and heat and relate them to changes in the internal energy of a system.
3. Explain the difference between path dependent variables and path independent variables.
4. Define enthalpy in terms of internal energy, pressure, and volume.

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5. Calculate First Law quantities such as q , w , ΔU and ΔH , for an ideal gas undergoing changes in temperature, pressure, and/or volume along isothermal, isobaric, isochoric, or adiabatic pathways.
6. Perform calculations using data collected using calorimetry (at either constant pressure or constant volume).
7. Write a formation reaction (the reaction for which the standard enthalpy of formation is defined) for any compound.
8. Use enthalpies of formation to calculate reaction enthalpies.
9. Estimate reaction enthalpies from average bond dissociation enthalpies.
10. Define and utilize enthalpies for phase changes such as ΔH_{fus} , ΔH_{sub} , and ΔH_{vap} to calculate the heat energy transferred in the corresponding phase change processes.
11. Define important thermodynamic functions such as ionization energy, electron affinity, bond dissociation energy, and lattice energy. Construct a Born-Haber cycle diagram using these values to describe the formation of an ionic crystalline compound.

Problems

1. In the attempt to measure the heat equivalent of mechanical work (as Joule did in his famous experiment) a student uses an apparatus similar to that shown below:



The 1.50 kg weight is lifted 30.0 cm against the force due to gravity (9.8 N). If the specific heat of water is $4.184 \frac{\text{J}}{\text{g}^\circ\text{C}}$, what is the expected temperature increase of the 1.5 kg of water in the canister?

2. 1.00 mol of an ideal gas, initially occupying 12.2 L at 298 K, expands isothermally against a constant external pressure of 1.00 atm until the pressure of the gas is equal to the external pressure. Calculate Δp , q , w , ΔU , and ΔH for the expansion.
3. Consider 1.00 mol of an ideal gas expanding isothermally at 298 K from an initial volume of 12.2 L to a final volume of 22.4 L. Calculate Δp , q , w , ΔU , and ΔH for the expansion.
4. Consider 1.00 mol of an ideal gas ($C_V = 3/2 R$) occupying 22.4 L that undergoes an isochoric (constant volume) temperature increase from 298 K to 342 K. Calculate Δp , q , w , ΔU , and ΔH for the change.

- Consider 1.00 mol of an ideal gas ($C_p = 5/2 R$) initially at 1.00 atm that undergoes an isobaric expansion from 12.2 L to 22.4 L. Calculate ΔT , q , w , ΔU , and ΔH for the change.
- Consider 1.00 mol of an ideal gas ($C_v = 3/2 R$) initially at 12.2 L that undergoes an adiabatic expansion to 22.4 L. Calculate ΔT , q , w , ΔU , and ΔH for the change.
- Derive an expression for the work of an isothermal, reversible expansion of a gas that follows the equation of state (in which a is a parameter of the gas)

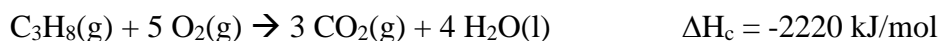
$$pV = nRT - \frac{an^2}{V}$$

from V_1 to V_2 .

- Use the following data [Huff, Squitieri, and Snyder, *J. Am. Chem. Soc.*, **70**, 3380 (1948)] to calculate the standard enthalpy of formation of tungsten carbide, $WC(s)$.

Reaction	ΔH° (kJ)
$C(gr) + O_2(g) \rightarrow CO_2(g)$	-393.51
$WC(s) + 5/2 O_2(g) \rightarrow WO_3(s) + CO_2(g)$	-1195.79
$W(s) + 3/2 O_2(g) \rightarrow WO_3(s)$	-837.42

- The standard molar enthalpy of combustion (ΔH_c) of propane gas is given by



The standard molar enthalpy of vaporization (ΔH_{vap}) for liquid propane



- Calculate the standard enthalpy of combustion of liquid propane.
 - Calculate the standard internal energy change of vaporization (ΔU_{vap}) for liquid propane.
 - Calculate the standard internal energy change of combustion (ΔH_c) for liquid propane.
- The enthalpy of combustion (ΔH_c) of aluminum borohydride, $Al(BH_4)_3(l)$, was measured to be -4138.4 kJ/mol [Rulon and Mason, *J. Am. Chem. Soc.*, **73**, 5491 (1951)]. The combustion reaction for this compound is given by



Given the following additional data, calculate the enthalpy of formation of $Al(BH_4)_3(g)$.

$\text{Al}_2\text{O}_3(\text{s})$	$\Delta H_f = -1669.8 \text{ kJ/mol}$
$\text{B}_2\text{O}_3(\text{s})$	$\Delta H_f = -1267.8 \text{ kJ/mol}$
$\text{H}_2\text{O}(\text{l})$	$\Delta H_f = -285.84 \text{ kJ/mol}$
$\text{Al}(\text{BH}_4)_3(\text{l})$	$\Delta H_{\text{vap}} = 30.125 \text{ kJ/mol}$

11. The standard enthalpy of formation (ΔH_f°) for water vapor is -241.82 kJ/mol at 25°C . Use the data in the following table to calculate the value at 100°C .

Substance	$C_p (\text{J mol}^{-1} \text{K}^{-1})$
$\text{H}_2(\text{g})$	28.84
$\text{O}_2(\text{g})$	29.37
$\text{H}_2\text{O}(\text{g})$	33.58

12. For a reaction $2 \text{A} \rightarrow \text{A}_2$, $\Delta H_{298} = -5.00 \text{ kJ}$. The change in constant pressure heat capacity is given by

$$\Delta C_p = 1 + bT$$

where $a = 1.00 \text{ J/K}$ and $b = 2.00 \times 10^{-3} \text{ J/K}^2$. Find the temperature at which $\Delta H = 0$.

13. From the following data, determine the lattice energy of BaBr_2 .

$\text{Ca}(\text{s}) \rightarrow \text{Ca}(\text{g})$	$\Delta H_{\text{sub}} = 129 \text{ kJ/mol}$
$\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$	$\Delta H_{\text{vap}} = 31 \text{ kJ/mol}$
$\text{Br}_2(\text{g}) \rightarrow 2 \text{Br}(\text{g})$	$D(\text{Br}-\text{Br}) = 193 \text{ kJ/mol}$
$\text{Ca}(\text{g}) \rightarrow \text{Ca}^+(\text{g}) + \text{e}^-$	$1^{\text{st}} \text{ IP(K)} = 589.8 \text{ kJ/mol}$
$\text{Ca}^+(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g}) + \text{e}^-$	$2^{\text{nd}} \text{ IP(K)} = 1145.4 \text{ kJ/mol}$
$\text{Br}(\text{g}) + \text{e}^- \rightarrow \text{Br}^-(\text{g})$	$1^{\text{st}} \text{ EA(Br)} = 194 \text{ kJ/mol}$
$\text{Ca}(\text{s}) + \text{Br}_2(\text{l}) \rightarrow \text{CaBr}_2(\text{s})$	$\Delta H_f = -675 \text{ kJ/mol}$

14. Using average bond energies

(http://chem.libretexts.org/Reference/Reference_Tables/Thermodynamics_Tables/T3%3A_Bond_Energies) estimate the reaction enthalpy for the reaction

