Chemical Thermodynamics Survival Kit

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1 First Law of Thermodynamics

The first law crops up everywhere you turn. Always remember it and, even more important, *remember to use it*!

$$\Delta U = q + w, \tag{1}$$

where ΔU is the internal energy, q is the heat, and w is work.

In *our* convention, if q is a positive number, it means the heat is being absorbed by the system (heat gain) and if it is a negative number, heat is being given out (heat loss). Also, in the same convention, if w is a positive number, the work is being done on the system ("work gain"), and if it is a negative number, the work is being done by the system ("work loss").

Internal energy of a system is a state property, i.e., it depends only on the initial and final states of the process and not on the actual path taken. The heat q and work w, on the other hand, do depend explicitly on the path taken from the initial to the final state. It is fascinating that two path dependent quantities can add up to give rise to a quantity that is independent of the path.

1.1 Internal Energy and Enthalpy

By definition,
$$dU = C_V dT. \tag{2}$$
If C_V is a constant independent of temperature (as in the case of an ideal gas), we may write $\Delta U = C_V \Delta T$. It follows that for an isothermal process involving an ideal gas, $\Delta U = 0$.

Another state property of interest to us is the *enthalpy* of the system, defined as
$$H = U + PV. \tag{3}$$
The change in enthalpy for an ideal gas undergoing a process can be written as
$$\Delta H = \Delta U + \Delta (PV) = \Delta U + \Delta (nRT). \tag{4}$$
From Eqs. (2) and (3), a change in enthalpy can also be defined as
$$dH = C_P dT, \tag{5}$$
using the relationship
$$C_P - C_V = nR. \tag{6}$$
Remember also that for an ideal gas, $C_{V,m} = \frac{3}{2}R$, which means that $C_{P,m} = C_{V,m} + R = \frac{5}{2}R$ where the subscript 'm' denotes a molar quantity.

1.2   Work

For our purposes, the most common form of work is that of the pressure-volume type. For example, expansion of a gas against an external pressure, or a phase change accompanied by a change in volume. This type of work is defined as

$$dw = -PdV \tag{7}$$

where the negative sign is inserted to conform the definition to the convention described below Eq. (1). If the external pressure, against which the work is done, is a constant, we can write

$$w = \int dw = -\int_{V_i}^{V_f} P_{\text{ext}} dV = -P_{\text{ext}}(V_f - V_i). \tag{8}$$

If the external pressure changes continuously with the expansion, as in the case of a reversible process, we must express P in terms of the other two variables of a gas, namely, V and T. An equation of state is required for this. For example, for an ideal gas undergoing an isothermal process, we write

$$w = -\int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln \left(\frac{V_f}{V_i} \right) = nRT \ln \left(\frac{P_f}{P_i} \right). \tag{9}$$

On the other hand, if the gas obeyed, say, the van der Waals equation of state, we would get

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2},$$

which, when inserted into the integral for calculating w, gives

$$w = -\int_{V_i}^{V_f} \left(\frac{nRT}{V - b} - \frac{n^2 a}{V^2} \right) dV = -nRT \ln \left(\frac{V_f - nb}{V_i - nb} \right) - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right). \tag{10}$$

1.3   Heat

There are two basic ways to find the amount of heat involved in a certain process. One is to check whether the process is at constant volume or constant pressure, *and* if no mechanical work is done. If so,

$$dq_V = nC_{V,m}dT \text{ (constant volume, } w = 0.) = dU \tag{11}$$
$$dq_P = nC_{P,m}dT \text{ (constant pressure, } w = 0.) = dH$$

The other method, which has to be used when $w \neq 0$, is to find ΔU and w for the process and then use the first law of thermodynamics.

1.4   Enthalpy changes

The quantity $C_{P,m}$ is a temperature-dependent quantity for most real (i.e., nonideal) gases and a number of liquids and solids. It is usually expressed in the form

$$C_{P,m} = d + eT + fT^{-2}, \tag{12}$$

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where the constants a, b and c have been tabulated for most substances. Finding enthalpy change using this expression, of course, involves the following integral:
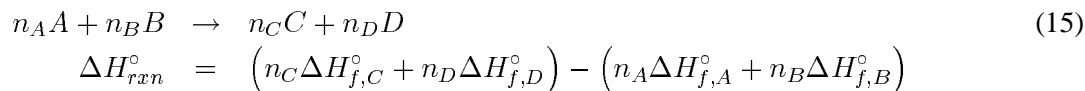
$$\Delta H_m = \int_{T_i}^{T_f} (d + eT + fT^{-2})dT \tag{13}$$

$$= d(T_f - T_i) + \frac{e}{2}(T_f^2 - T_i^2) - f\left(\frac{1}{T_f} - \frac{1}{T_i}\right)$$

This can be used to find the enthalpy change for a process at a given temperature T_2 if we already know the value of the enthalpy change at another temperature T_1:

$$\Delta H_{m,T_2} = \Delta H_{m,T_1} + d(T_2 - T_1) + \frac{e}{2}(T_2^2 - T_1^2) - f\left(\frac{1}{T_2} - \frac{1}{T_1}\right). \tag{14}$$

1.5   Enthalpy of a reaction

As you have learned in Freshman Chemistry, the standard enthalpy of a reaction can be found from the enthalpies of formation of the reactants and products, as in the reaction

$$n_A A + n_B B \rightarrow n_C C + n_D D \tag{15}$$

$$\Delta H_{rxn}^\circ = \left(n_C \Delta H_{f,C}^\circ + n_D \Delta H_{f,D}^\circ\right) - \left(n_A \Delta H_{f,A}^\circ + n_B \Delta H_{f,B}^\circ\right)$$

where the superscript "$\circ$" signifies that the reactants and products are all in their standard states. The enthalpy of a reaction at a temperature other than the standard temperature T° (usually 298 K) can be found by using Eq. (14) to find the enthalpies of formation of all the reactants and products at the desired temperature, and then using a relationship similar to that in Eq. (15). Otherwise, we could define the changes in the a, b, c parameters appearing in the $\overline{C}_P$ of the reactants and products due to the reaction, as

$$\Delta d = (n_C d_C + n_D d_D) - (n_A d_A + n_B d_B) \tag{16}$$

$$\Delta e = (n_C e_C + n_D e_D) - (n_A e_A + n_B e_B)$$

$$\Delta f = (n_C f_C + n_D f_D) - (n_A f_A + n_B f_B)$$

and then use these quantities to define the enthalpy of reaction at the new temperature T, $\Delta H_{rxn}^{(T)}$:

$$\Delta H_{rxn}^{(T)} = \Delta H_{rxn}^\circ + \Delta d(T - T^\circ) + \frac{\Delta e}{2}(T^2 - T^{\circ 2}) - \Delta f\left(\frac{1}{T} - \frac{1}{T^\circ}\right). \tag{17}$$

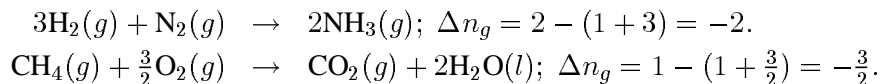## 1.6   Relation between enthalpy and internal energy

The enthalpy for a reaction in which gases are involved can be related to the internal energy change for the reaction simply by using Eq. (4) and substituting for the term PV appropriately. For example, taking the case of the reaction above (assuming that A, B, C, and D are all gases) and using the ideal gas law,

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT).$$

If the reaction takes place at a constant temperature, the only quantity that can change during the reaction is the number of moles of gases. Therefore, we write

$$\Delta H = \Delta U + \Delta n_g RT, \tag{18}$$

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where $\Delta n_g = (n_C + n_D) - (n_A + n_B)$. If any one of these species is not a gas, that species will have to be dropped from consideration. So, for example,

$$3H_2(g) + N_2(g) \quad \rightarrow \quad 2NH_3(g); \ \Delta n_g = 2 - (1 + 3) = -2.$$
$$CH_4(g) + \tfrac{3}{2}O_2(g) \quad \rightarrow \quad CO_2(g) + 2H_2O(l); \ \Delta n_g = 1 - (1 + \tfrac{3}{2}) = -\tfrac{3}{2}.$$

In the second case, the combustion of methane, the water formed is in the liquid state and, therefore, the number of moles of water is not taken into consideration (obviously, the ideal gas law cannot be applied to a liquid).

2   Second Law of Thermodynamics

One of the many ways of stating the second law of thermodynamics is that it is impossible to transfer heat from a cold body to a hot body without performing work on the system. The concept of entropy, S, follows from the second law. Any change in which the entropy of the universe (system+surroundings) increases is a spontaneous or irreversible process. All natural processes that occur over a finite amount of time are irreversible. In order to find the entropy change of the universe ΔS_{univ} during a process, we need to find the entropy change of the system ΔS and the entropy change of the thermal surroundings ΔS_{surr} during the process.

2.1   Entropy change of the system

It turns out that the entropy change of the system, ΔS, is a state property, depending only on the initial and final states. Therefore, even if we do not know or cannot replicate the actual path the system took in order to get to the final state from a given initial state, we can always design any path we wish to connect the two and find ΔS along that path. It also turns out that ΔS can only be found along *reversible* paths. Therefore, we start with a definition of ΔS and look for ways to find it. The definition is

$$dS = \frac{dq_{rev}}{T}, \tag{19}$$

where the subscript "*rev*" on dq signifies that this is the heat absorbed (or evolved) during a reversible process. Since the entropy change for the system is a state property, and it is **by definition**, based on dq_{rev}, we must always evaluate dS using *a reversible path* that connects the initial and final states, *regardless of the nature of the actual process*! There are three types of processes we wish to consider: (1) a phase change under conditions such that the two phases are in equilibrium, (2) a reversible volume (or pressure) change for ideal gas, and (3) a reversible temperature change at constant volume or constant pressure.

2.1.1   Equilibrium Phase change

All phase changes occur at a fixed temperature and are accompanied by an enthalpy change, such as enthalpy of fusion, enthalpy of vaporization, enthalpy of sublimation. The entropy change for the system undergoing a phase change is defined as

$$\Delta S = \frac{n \Delta H_{m,pc}}{T_{pc}}. \tag{20}$$

If the actual process involves a phase change under conditions where the two phases are not in equilibrium (eg., freezing of water at -10°C), a reversible path must be constructed whereby the two phases are brought into equilibrium before the equation above can be used.

2.1.2 Reversible Volume (or Pressure) change

Consider an isothermal reversible expansion of an ideal gas. We already know that $dU = 0$ for this process. Therefore, $dq = -dw = PdV$. Therefore,

$$dS = \frac{PdV}{T},$$

and

$$\Delta S = \int_{S_i}^{S_f} dS = \int_{V_i}^{V_f} \frac{P}{T} dV.$$

Substituting for P using the ideal gas law, and integrating, we get

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) = nR \ln \left(\frac{P_i}{P_f} \right). \tag{21}$$

2.1.3 Reversible Temperature change

Let us consider a constant volume process. Since the volume is constant, no work is done and, therefore, $dU = dq$, or

$$dS = \frac{nC_{V,m}dT}{T},$$

which, if we assume that C_V is a constant independent of temperature, leads to

$$\Delta S = nC_{V,m} \int_{T_i}^{T_f} \frac{dT}{T} = nC_{V,m} \ln \left(\frac{T_f}{T_i} \right). \tag{22}$$

Similarly, for a constant pressure process, $dH = dq$, and a similar analysis leads to

$$\Delta S = nC_{P,m} \int_{T_i}^{T_f} \frac{dT}{T} = nC_{P,m} \ln \left(\frac{T_f}{T_i} \right). \tag{23}$$

Actual processes may not fall into any of these categories. However, we can always design paths connecting the initial and final states where a combination of these three types of processes are used, and we now have equations to calculate ΔS for each of them. By combining the last two processes, we can write general equations for processes involving gases, as

$$\Delta S = nR \ln \left(\frac{V_f}{V_i} \right) + nC_{V,m} \ln \left(\frac{T_f}{T_i} \right), \tag{24}$$

$$\Delta S = nR \ln \left(\frac{P_i}{P_f} \right) + nC_{P,m} \ln \left(\frac{T_f}{T_i} \right).$$

Note that if volumes appear in the first term, the second term must have a $C_{V,m}$ in it, and if the first term has pressures, the second term must have a $C_{P,m}$.

2.2 Entropy change of the surroundings

We must always use information about the *actual* process to find the entropy change of the thermal surroundings. If sufficient information is not provided about the surroundings, then this quantity cannot be calculated. This is a weakness of the entropy criterion for spontaneity. The entropy change of the surroundings are defined as

$$\Delta S_{surr} = \frac{-q_{act}}{T_{surr}} \tag{25}$$

where the quantity q_{act} is the heat absorbed or evolved from the system during the *actual* process (as opposed to the reversible path we have constructed between the initial and final states). The negative sign in front of q_{act} is inserted only to comply with our convention of considering a positive value of q_{act} as heat absorbed by the system during the *actual process* (which, amazingly enough, is irrelevant for calculating ΔS). From the point of view of the surroundings, when the system absorbs heat, the surroundings are losing heat and, therefore, the entropy change of the surroundings, ΔS_{surr}, must be negative.

2.3 Adiabatic Processes

An adiabatic process is one in which no heat is absorbed or given out. Therefore, by definition, $dS = 0$ for an adiabatic process and so, adiabatic processes are also known as *isentropic* processes. For an ideal gas undergoing an adiabatic expansion, the following relationships hold true:

$$
\begin{aligned}
V_i T_i^{C_{V,m}/R} &= V_f T_f^{C_{V,m}/R} \\
P_i V_i^{\gamma} &= P_f V_f^{\gamma}
\end{aligned}
\tag{26}
$$

where $\gamma = C_{P,m}/C_{V,m}$.

2.4 An Example

One mole of an ideal gas is initially at 10 bar and 298 K. It is allowed to expand against a constant external pressure of 2 bar to a final pressure of 2 bar. During this process, the temperature of the gas falls to 253.2 K. Find $\Delta U, \Delta H, \Delta S$, ΔS_{surr}, and ΔS_{univ} for the process. Assume that the thermal surroundings remain at 298 K throughout.

Recall that the entropy change for the system can be calculated only along a reversible path. There are obviously several reversible paths that can be constructed between the initial and final states in this case. Let us consider four of them. You must sketch these paths on a PV diagram so that you can visualize them.

2.4.1 Isothermal expansion to the final volume followed by constant volume cooling to the final temperature:

$$\Delta U = 0 + C_{V,m}\left(T_f - T_i\right) = \tfrac{3}{2}R(253.2 - 298) = -558.7 \text{ Joules mol}^{-1}$$

$$\Delta H = 0 + C_{P,m}\left(T_f - T_i\right) = \tfrac{5}{2}R(253.2 - 298) = -931.2 \text{ Joules mol}^{-1}$$

$$\Delta S = R\ln\left(\frac{V_f}{V_i}\right) + C_{V,m}\ln\left(\frac{T_f}{T_i}\right) = R\ln\left(\frac{10.526}{2.478}\right) + \tfrac{3}{2}R\ln\left(\frac{253.2}{298}\right) = 12.026 - 2.032 = 9.994$$
Joules K^{-1} mol^{-1}

2.4.2 Isothermal expansion to the final pressure followed by constant pressure cooling to the final temperature:

$$\Delta U = 0 + C_{V,m}\left(T_f - T_i\right) = \tfrac{3}{2}R(253.2 - 298) = -558.7 \text{ Joules mol}^{-1}$$

$$\Delta H = 0 + C_{P,m}\left(T_f - T_i\right) = \tfrac{5}{2}R(253.2 - 298) = -931.2 \text{ Joules mol}^{-1}$$

$$\Delta S = R\ln\left(\frac{P_i}{P_f}\right) + C_{P,m}\ln\left(\frac{T_f}{T_i}\right) = R\ln\left(\frac{10.0}{2.0}\right) + \tfrac{5}{2}R\ln\left(\frac{253.2}{298}\right) = 13.381 - 3.386 = 9.995$$
Joules K^{-1} mol^{-1}

2.4.3 Isothermal expansion to (P_0, V_0) followed by adiabatic expansion to the final state:

Note that we need to find the intersection of the isotherm that passes through the initial state and the adiabat that passes through the final state, which occurs at (P_0, V_0) at the temperature of the isotherm, i.e., at T_i. Using the relationships provided above for adiabatic processes, we get

$$V_0 T_i^{3/2} = V_f T_f^{3/2};$$

$$V_0 = 10.526L \times \left(\frac{253.2}{298.0}\right)^{3/2} = 8.244 \text{ L}$$

$$\Delta U = 0 + C_{V,m}\left(T_f - T_i\right) = \tfrac{3}{2}R(253.2 - 298) = -558.7 \text{ Joules mol}^{-1}$$

$$\Delta H = 0 + C_{P,m}\left(T_f - T_i\right) = \tfrac{5}{2}R(253.2 - 298) = -931.2 \text{ Joules mol}^{-1}$$

$$\Delta S = R\ln\left(\frac{V_0}{V_i}\right) + 0 = R\ln\left(\frac{8.244}{2.478}\right) = 9.994 \text{ Joules K}^{-1} \text{ mol}^{-1}$$

2.4.4 Constant pressure heating to the final volume followed by constant volume cooling to the final pressure:

The gas will have to be heated to $T_0 = 1266$ K in order for it to reach a volume of 10.526 L at 10 bar pressure. Therefore,

$$\Delta U = C_{V,m}\left(T_0 - T_i\right) + C_{V,m}\left(T_f - T_0\right) = \tfrac{3}{2}R(1266 - 298) + \tfrac{3}{2}R(253.2 - 1266) = -558.7 \text{ Joules}$$
mol^{-1}

$$\Delta H = C_{P,m}\left(T_0 - T_i\right) + C_{P,m}\left(T_f - T_0\right) = \tfrac{5}{2}R(1266 - 298) + \tfrac{5}{2}R(253.2 - 1266) = -931.2 \text{ Joules}$$
mol^{-1}

$$\Delta S = C_{P,m}\ln\left(\frac{T_0}{T_i}\right) + C_{V,m}\ln\left(\frac{T_f}{T_0}\right) = \tfrac{5}{2}R\ln\left(\frac{1266}{298}\right) + \tfrac{3}{2}R\ln\left(\frac{253.2}{1266}\right) = 9.995 \text{ Joules K}^{-1} \text{ mol}^{-1}$$

Yet another path you might try on your own is constant volume cooling to the final pressure followed by constant pressure heating to the final temperature.

In each of these cases, we have verified that $\Delta U, \Delta H, \Delta S$ are the same, thus proving that they are independent of the path taken, as any state property should be. We now have to find the entropy change of the surroundings.

2.4.5   Entropy change of the surroundings:

The actual process is the expansion of the gas against a constant external pressure of 2 bar. For this process, according to the first law,

$$\Delta U = q_{act} - P_{ext}(V_f - V_i).$$

Therefore, $q_{act} = \Delta U + P_{ext}(V_f - V_i) = -558.7 + 2.0(10.526 - 2.478) \times \dfrac{8.3143}{0.083143}$ Joules mol^{-1} = 1050.9 Joules mol^{-1}.

Now, using the definition of ΔS_{therm}, we get

$$\Delta S_{surr} = -q_{act}/T_{surr} = -1050.9 \text{ Joules mol}^{-1}/298 \text{ K} = -3.526 \text{ Joules K}^{-1} \text{ mol}^{-1}.$$

Therefore, $\Delta S_{univ} = \Delta S + \Delta S_{surr} = 6.468$ Joules K^{-1} mol^{-1}.

This is, therefore, a spontaneous process.