THERMODYNAMIC CONCEPTS: SOME CONSIDERATIONS ON THEIR USE IN INTRODUCTORY COURSES OF CHEMISTRY

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Abstract

Most phenomena described in introductory university courses of chemistry have a solid thermodynamic conceptual foundation. It is unavoidable, at this initial level, to treat thermodynamic concepts partially (especially the second principle), and to use examples and applications corresponding to very definite and simple cases. In these conditions, great care must be exerted to help students avoid the misconceptions that they frequently adopt after being exposed to this partial vision of thermodynamics.

The following are the most frequent ones: 1) to incorrectly extend to all isothermal processes in any system, the conclusion that the internal energy change is null for all isothermal expansion-compression processes of an ideal gas, 2) to unrestrictedly associate enthalpy changes with transferred thermal energy, 3) to unrestrictedly use free energy changes as spontaneity criteria. We discuss here how these false interpretations commonly develop, and propose possible alternatives to decrease their frequency.

Resumen

La termodinámica es una herramienta fundamental en cualquier curso universitario inicial de química ya que constituye una base conceptual sólida sobre la cual se pueden justificar los aspectos fenomenológicos de diversos temas. Naturalmente, en el nivel inicial, la termodinámica, y especialmente el segundo principio, son tratados sólo parcialmente, con la consecuencia de que los ejemplos y aplicaciones suelen corresponder a casos muy particulares y sencillos que no sólo transmiten una visión incompleta sino que, con frecuencia, suelen conducir a desconceptos o a errores de interpretación por parte de los alumnos. Entre estos últimos, podemos enumerar los siguientes: 1) la extensión errónea de una variación de energía interna nula a procesos distintos de la expansión-compresión isotérmica de un gas ideal, 2) la asociación sin restricciones de la variación de entalpía al calor puesto en juego en un proceso y 3) el uso de la variación de energía libre como criterio de espontaneidad sin restricciones.

En este trabajo, presentaremos éstos y otros ejemplos en los cuales suelen detectarse falsas interpretaciones además de una discusión sobre posibles alternativas para disminuir la frecuencia y la incidencia de estos desconceptos.

Introduction

Thermodynamics is a solid conceptual foundation for many phenomena (e.g., chemical and phase equilibrium, electrochemistry) described in initial university courses of chemistry, but many introductory textbooks deal with the complex and subtle thermodynamic concepts at a very superficial level, frequently presenting and describing them without any reference to examples or applications, or applied only to very simple or very specific systems [1-6]. A very incomplete overview of thermodynamics is thus transmitted to the student. Misconception and interpretation errors are easily generated in this context.

In this work, we will describe some commonly encountered false interpretations, and discuss possible alternatives to reduce their prevalence.
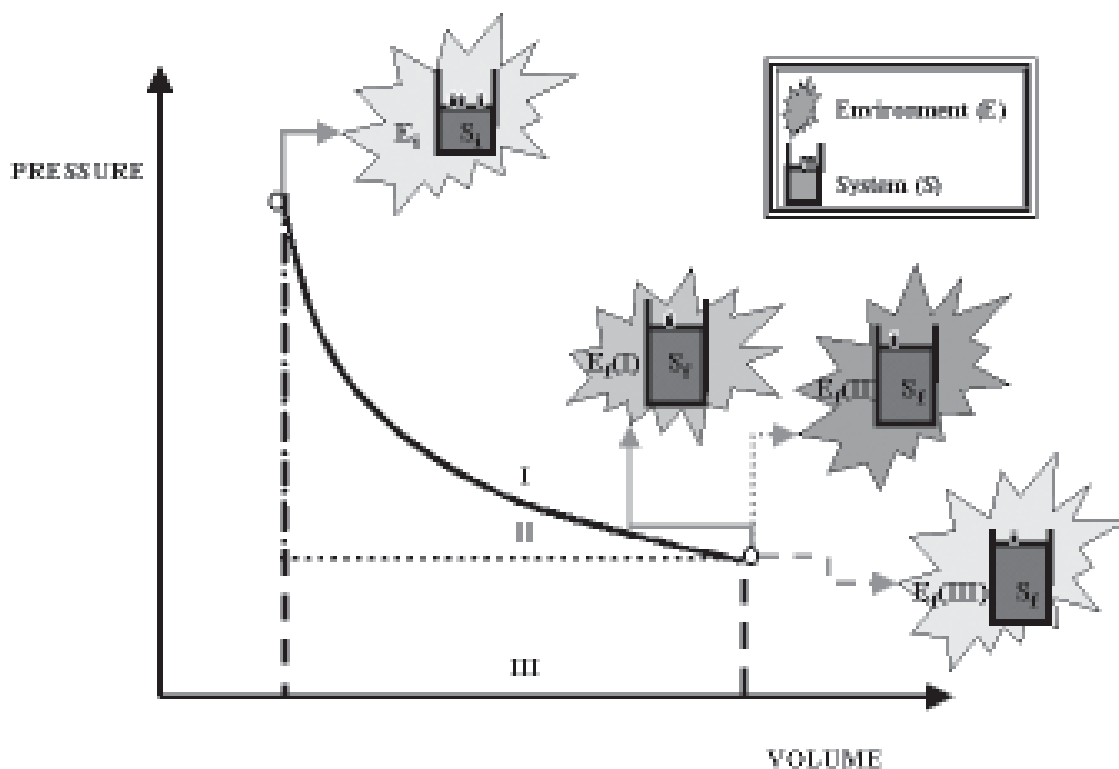

Figure 1

Isothermal expansion of an ideal gas

The isothermal expansion of an ideal gas (figure 1) is usually the single example for which all (or almost all) thermodynamic variables and state functions are calculated. The system is sufficiently simple and clarifying to be didactically profitable. But it is also extremely singular and, if this is not pointedly stressed and discussed in detail, students are apt to fall into erroneous extrapolations that clash against thermodynamic principles. Some of the most common erroneous statements are quoted and commented below.

1) "The internal energy change (ΔE(system) is zero for all isothermal processes"

This is absolutely correct in the case of ideal gases, since their internal energy (E) is completely determined by their thermal state. However, students frequently extrapolate this to any isothermal process in real gases, liquids or solids and, even, to ideal gases in nonisothermal processes. Consequently, it must be emphasized that E is a function of the volume (V) and the temperature (T):

$$dE = (\delta E/\delta T)_V dT + (\delta E/\delta V)_T dV = Cv\ dT + (\delta E/\delta V)_T dV \tag{1}$$

where Cv is the molar heat capacity at constant volume [7]. It is clear from (1) that dE can only be zero for an isothermal process if $(\delta E/\delta V)_T$ is zero, as is for an ideal gas, but not for real gases, solids or liquids.

In basic courses, it will be sufficient to insist on the impossibility for the internal energy of an ideal gas to change when the gas volume changes, because of the lack of interaction forces. For an advanced course, the use of the thermodynamic equation of state, valid for any aggregation state [7-8].

$$P\ (pressure) = T(\delta P/\delta T)_V - (\delta E/\delta V)_T \tag{2},$$

will show that, if the equation of state for an ideal gas holds, $\delta P/\delta T$ equals R/V for one mole of ideal gas, and then $(\delta E/\delta V)_T$ must be zero.

2) "The enthalpy change (Δ H(system)) in the isothermal expansion of an ideal gas equals the absorbed heat."

The error arises because the students, recently trained in the thermochemical applications of the first principle, where ΔH equals the absorbed thermal energy at the usual conditions of constant pressure and temperature and only expansion-compression (*PV*) work), do not remember these restrictions or fail to see that they do not apply to this case.

In fact, they are usually surprised when they are shown that for this transformation $\Delta H = 0$. An even greater surprise might be caused if, following Granville [8], we showed them that an "endothermic" reaction can have a negative enthalpy change.

The conditions in which ΔH(system) can be identified with the thermal energy absorbed by the system (δq) can be clarified through a careful analysis of the definition of enthalpy, as

$$dH = d(H+PV) = dE + d(PV) = \delta q - \delta w_T + d(PV) \tag{3},$$

where δw_T is the total work done by the system. With the restriction of constant pressure

$$dH = \delta q - \delta w_T + PdV \tag{4},$$

and separating w_T into *PV* work (δw_{PV}) and all other possible forms of work that the system

might perform (δw_{other}),

$$dH = \delta q - (\delta w_{PV} + \delta w_{other}) + PdV \tag{5}$$

$$dH = \delta q - PdV - \delta w_{other} + PdV = dH = \delta q - \delta w_{other} \tag{6}$$

Thus, only at constant pressure and when all work is *PV* work ($w_{other} = 0$) is

$$dH = \delta q \tag{7}$$

The example of isothermal *PV* changes of an ideal gas system is, because of its directness, very appropriate to show that the change in state functions is the same for all paths, and that other magnitudes, such as heat and work, undergo different changes along different paths. This is normally shown to the student by the consideration of several paths for the change from an initial to a final state (see figure 1): I, reversible; II, expansion against the final pressure; III, expansion against vacuum. However, when the entropy change of the universe is calculated along these paths, for which the initial and final states of the system are the same, the following correct conclusion usually surprises the students, who consider it erroneous.

3) "The entropy change of the environment ($\Delta S(environment)$) is different for each different path of the system from the same initial to the same final state."

The students have been trained to calculate state functions along one path (the most convenient or, in the case of entropy, the reversible path), since the results will be valid for all paths, which is, of course, quite correct. However, when faced with the entropy change of the environment for reversible or irreversible changes in the system, they might fail to realize that the final states of the environment differ in each case. If the students fall for this error, they will erroneously conclude that ΔS of the universe is the same for reversible or irreversible paths. To avoid this pitfall, it may be necessary to conduct a class discussion over the concepts of "universe," "system" and "environment." These are usually introduced at the beginning of the lectures on thermodynamics but, without concrete examples, they become abstract definitions for the student. A class discussion at this point should make clear that:

The universe is the group of everything related to (or affected by) the changes taking place in the system. In this particular case, the environment is a source or a sink of thermal energy. It can be chosen large enough and in contact for such a long time that, once the changes in the system are over, the environment is in equilibrium and its temperature does not differ sensibly from the initial state. That is to say, the environment can arbitrarily be chosen so big that it does not undergo any variations in its thermodynamic variables (P, T) irrespective of what happens to the system. In these conditions, any process taking place in such a correctly selected environment will be thermodynamically reversible.

When paths I, II and III (figure 1) are analyzed, the interaction of the environment with the system will be different in each case and the transferred thermal energy will differ for each path, specifically: $-nRT\ln(V_f/V_i)$ along path I; $P_f(V_f-V_i)$ along path II, and zero along path III.

4) Other miscellaneous misconceptions involving ΔG, equilibrium and spontaneity in the isothermal expansion of an ideal gas.

Since the process is isothermal

$$\Delta G = \Delta H - T\Delta S \tag{8},$$

replacing $\Delta H = 0$ and $\Delta S = Q_{REV}/T$

$$\Delta G = -Q_{REV} \tag{9}.$$

Since Q_{REV} (reversibly absorbed heat) is positive, $\Delta G < 0$ for all pathways between the same initial and final states. Some students conclude from this fact that the expansion processes (I, II and III, figure 1) are spontaneous because "the free energy of the system decreases." Paradoxically, other students argue that for the reversible path I, which is a succession of quasi-equilibrium states, ΔG should be zero, as is for a system in equilibrium.

Again, a class discussion on the restrictions of ΔG as a spontaneity criterion is in order. The reasons to use ΔG(system), rather than ΔS(universe) as a spontaneity criterion should also be discussed. The common conclusion of the discussion of this second point is that the processes that interest the chemists usually take place at constant pressure and temperature, and also, that the calculation of ΔS(universe) is usually more complex especially because of the calculation of ΔS(environment). However, in the only example normally discussed (*PV* processes in an ideal gas system), the calculation of ΔS(environment) is not very difficult, and to make matters worse, ΔG (system) is not valid as a spontaneity criterion. These are powerful reasons to include another example that could be comprehensively discussed. This discussion should enlighten the difficulties stated above.

Changes of state

A good candidate for such an example is any chemical process. However, for students in the initial university level, it is probable that the complexity of the example hinders the proposed objective. Alternatively, the physical process of a change in aggregation state (used in some textbooks almost always in connection with the first principle) is a simpler and still effective system to broaden the exemplification of the concepts of the second principle, because:

a) It is easily shown that for this isothermal process ΔE cannot be null.

If equations (3)-(7) applied to an equilibrium change of state of a pure substance, where *P* and *T* are constant and only *PV* work is performed, let us conclude that $dH = q$, or, integrating

$$\Delta H = Q \tag{10}$$

Choosing a specific system for the analysis, e.g., the melting of 1 mole of ice at 0 ºC and 1 atm

$$\Delta H = m\ L_{f} = (18\ \text{g/mole})\ (80\ \text{cal/g}) = 1440\ \text{cal/mole} \tag{11},$$

where L_f is the enthalpy of fusion. Therefore, at constant pressure

$$dH = dE + P\ dV \tag{12},$$

and integrating,

$$\Delta H = \Delta E + P\ \Delta V \tag{13}$$

Thus, $\Delta E = \Delta H - P\ \Delta V = m\ L_f - P\ \Delta V$ can hardly be zero, since $P\ \Delta V$ is very small (as the students can readily calculate, given the respective densities of ice and water). In our particular case, the variation of volume is practically zero, so

$$\Delta H \cong \Delta E \cong 1440\ \text{cal/mole} \tag{14}$$

b) Analysis of entropy changes of the system and of the environment: When ice melts at exactly 0 ºC and 1 atm, the process is reversible and

$$\Delta S = \Delta H_{(f)}^{273}/273\ \text{K} = 5.275\ \text{cal/ K mole} \tag{15}$$

Clearly, ΔS(environment) will be –5.275 cal/Kmole and ΔS(universe) = 0. It is illustrative to calculate ΔS for irreversible paths, for example, for the melting of 1 mole of ice at 274 K. To calculate the entropy changes, we should follow reversible paths, that is, for the system: cool reversibly 1 mole of ice from 274 K to 273 K, melt it reversibly at 273 K (ΔS = 5.275 cal/K.mole, as calculated in (15), above), and heat 1 mole of water reversibly from 273 K to 274 K. The entropy changes for the cooling and heating processes are calculated from

$$\Delta S = m\ c_{p} \ln(T_{f}/T_{i}) \tag{16},$$

where m stands for the mass (one mole in this case) and c_p is the specific heat capacity. The results are: ΔS(ice cooling) = -0.033; ΔS(water heating) = 0.066 cal/K.mole; ΔS(system) = 5.308 cal/K mole.

To calculate ΔS(environment), we should consider that the environment has reversibly transferred the thermal energy necessary for the fusion at 274 K. Thus, ΔS(environment) = (-1440 cal/mole) / 274 K. = -5.255 cal/K.mole (rigorously, the latent heat of fusion at 274K, estimated as described in the appendix, should be used in this calculation). The result shows that ΔS(universe) > 0, as expected for an irreversible process.

It is interesting to discuss the entropy changes for the imaginary process in which one mole of ice melted/melts at 272 K. To calculate ΔS(system), the following reversible path should be used: one mole of ice is cooled from 273 to 272 K, melted at 272 K to water at 272 K, and the water heated to 273 K. Supposing that the latent heat of fusion is constant,

ΔS(system) = 5.242 cal/ K.mole, while ΔS(environment) = –5294 cal/ K.mole. Thus, ΔS(universe) < 0 and the process will not take place.

c) Use of ΔG as spontaneity criterion. The employment of ΔG as a spontaneity criterion is correct for this example (*P* and *T* are constant). It is also rapidly observed that it is much simpler than the ΔS(universe) > 0 criterion. Using equation (8) (and assuming that neither ΔH_{fusion} nor ΔS_{fusion} change appreciably between 274 and 272 K) it can be calculated that

$$\Delta G_{272} = 1440 \text{ cal/mole} - 272 \text{ K } 5.275 \text{ cal/Kmole} = 5.27 \text{ cal/mole}$$

indicating a nonspontaneous process,

$$\Delta G_{272} = 1440 \text{ cal/mole} - 273 \text{ K } 5.275 \text{ cal/Kmole} = 0$$

indicating an equilibrium (reversible) process,

$$\Delta G_{272} = 1440 \text{ cal/mole} - 274 \text{ K. } 5.275 \text{ cal/K.mole} = -5.35 \text{ cal/mole}$$

indicating a spontaneous (real) process,

Conclusion

In initial university courses, changes in all thermodynamic state functions are usually calculated only for the reversible isothermal expansion of an ideal gas. Owing to the very specific characteristics of this system, the students are prone to extract several false interpretations and erroneous extrapolations. We suggest including an additional example, a change of state, which, by itself, is also incomplete and can also promote incorrect interpretations. Nevertheless, a comparison between the changes in the same state functions in both examples, carefully considering differences and restrictions, should generate a deeper and more complete understanding of the topic. In particular, the PV processes in an ideal gas are appropriate to:

1. highlight that heat and work are not state functions and that different values are obtained for different transformation pathways.
2. differentiate reversible and irreversible processes.
3. demonstrate that when the system transforms from one initial state to the same final one, through different pathways, the environment should necessarily reach different final states.

The changes in the aggregation state process, on the other hand,

1. provides a different example of the use of ΔS(universe) as a predictive tool, helping students apprehend this difficult concept.
2. allows to better appreciate ΔG(system), at constant P and T and only PV work, as a convenient criterion of spontaneity.
3. presents enthalpy as it is frequently found in chemical processes

Focusing in the comparison between the examples will help decrease the incidence of inadequate generalizations and give the students the opportunity to appreciate the importance of the restrictions in the calculation of thermodynamic magnitudes and, furthermore, in the physical meaning of some of these magnitudes. The comparison and discussion can be carried out without great difficulty at different levels of mathematical rigor, according to the level of the course.

APPENDIX: Calculation of the latent heat at different temperatures
According to the Kirchhoff equation

$$[d(\Delta H)/dT]_{\mathrm{P}} = \Delta C_{\mathrm{p}} \tag{17}.$$

Integrating (17), with the assumption that, for a small temperature interval, Cp is independent of temperature

$$\Delta H_{\mathrm{Tf}} = \Delta H_{\mathrm{Ti}} + \Delta C_{\mathrm{p}}.\Delta T \tag{18}.$$

For the melting of a mass of ice, m, as in the example treated above,

$$\Delta H_{\mathrm{(f)274}} = \Delta H_{\mathrm{(f)273}} + m(c_{\mathrm{pliq}} - c_{\mathrm{psol}})\Delta T \tag{19}.$$

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