Student Misconceptions in Thermodynamics

Mark F. Granville
University of Connecticut, Storrs, CT 06268

Several decades ago general chemistry and physical chemistry textbooks contained few, if any, problems with solutions as part of the text. Today, it is not uncommon to find one of these "examples" on every other page. As S.A.T. scores and math abilities decreased, educators responded by increasing the emphasis on problem-solving and the methodology of problem-solving. We often tell our students that working problems is an effective way to study. What we have in mind is that working problems gives the student a structure within which to review the principles contained in the course material. Unfortunately, the students respond by adopting the attitude that arriving at an answer is more important than understanding the problem. They learn to look for certain key words that link the problem at hand with one they have already seen. In an attempt to find a quick and easy solution, they often misuse the implications of these key words to the extent that a clear review of the principles involved is lost.

The following misconceptions, with the associated keyword in italics, seem to be particularly common among students who have finished a one-semester, junior-level course in chemical thermodynamics. When presented as a series of true/false questions, these statements are usually judged to be true although each requires at least one more condition be satisfied. A classroom discussion of these points at the end of the semester is an effective method of stimulating the students to think about the basic concepts in a problem before proceeding to a solution. The text following each statement is a condensed version of the presentation I have used with several of my undergraduate classes. The additional conditions needed to make the statement applicable appear in italics.

$\Delta E = 0$ for an *Isothermal* Process

This is true for an *ideal gas*. The ideal gas is used so extensively in the development of the First Law of Thermodynamics that this incorrect generalization becomes firmly established before other cases are examined. If we consider energy to be a function of temperature and volume then

$$dE = C_V dT + (\partial E/\partial V)_T dV$$

where $C_V = (\partial E/\partial T)_V$. For ideal gases, $(\partial E/\partial V)_T = 0$, so $dE = C_V dT$ and $\Delta E = 0$ for an isothermal process. This is usually presented as a property of ideal gases (Joule experiment) even before establishing it through the Second Law. Using the Second Law, we derive the thermodynamic equation of state

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P$$

For an ideal gas, $(\partial P/\partial T)_V = P/T$ and $(\partial E/\partial V)_T = 0$. This is not true for solids, liquids, and real gases. For example, a Van der Waals fluid has $(\partial E/\partial V)_T = a/\bar{V}^2$ (which is calculated in a homework problem but long since forgotten) so a change in volume will result in a change in energy even if the temperature is constant.

It should be noted that other equations of state can also lead to $dE = C_V dT$ to avoid another misconception, viz., that $(\partial E/\partial V)_T = 0$ only for ideal gases. Any gas with the equation of state $P = RTf(\bar{V})$, where $f(\bar{V})$ is a function only of volume, will behave like an ideal gas in First Law calculations.[1]

$\Delta S = 0$ for an *Adiabatic* Process

This is true if the process is *reversible*. If the process is irreversible, then $\Delta S > 0$. So much importance is put on the fact that the integrals of dU, dH, and dS are path independent, i.e., they are exact differentials, that the students tend to forget the path must be reversible when integrating $dS = dQ_{rev}/T$. They recognize that $\int dQ$ is path dependent but do not understand why all paths are not acceptable for dQ_{rev}/T since dS is exact. The significance of the "rev" subscript is lost even though it is carefully explained in the development of the Second Law.

$\Delta S > 0$ for a *Spontaneous* Process

This is a problem of nomenclature. When the Clausius inequality is first introduced, ΔS refers to the *system + surroundings* or to an *isolated* system. However, after the concept of Gibbs Energy is developed ΔS usually refers to the system only, isolated or not. The following problem, adapted from a well-known textbook[2] illustrates this point nicely.

The heat of fusion of mercury is 2368 J/mol at its melting point of $-39°C$, and the heat capacities of solid and liquid mercury are both 27.9 J/K-mol. Calculate ΔS and ΔG for the irreversible process

$$Hg(l, -50°C) \rightarrow Hg(s, -50°C)$$
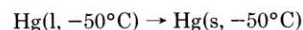
Since the heat capacity is the same for both phases, the calculation is straightforward:

$$\Delta S_{223} = \Delta S_{234} = -\Delta H_{fus}/T_m = -10.1 \text{ J/K-mol}$$

Many students either leave out the negative sign (forgetting that ΔH_{fus} refers to s $\rightarrow$ l) or change the answer to positive. Since this is certainly a spontaneous process, ΔS clearly cannot be less than 0. In order to carry out the freezing isothermally, the mercury cannot be isolated from the surroundings. The heat given off upon freezing must be absorbed by the surroundings. Since this takes place at $-50°C$, the entropy change of the surroundings is

$$\Delta S_{surr} = \Delta H_{fus}/T_{223} = +10.6 \text{ J/K-mol}$$

The *total* entropy change of this process is thus positive:

$$\Delta S_{total} = \Delta S_{surr} + \Delta S_{Hg} = +0.5 \text{ J/K-mol}$$

The sign of the Gibbs Energy change should, of course, reflect the spontaneity of the process. Again, since the heat capacity does not change,

$$\Delta H_{223} = \Delta H_{234} = -\Delta H_{fus}$$

and

$$\Delta G_{223} = \Delta H_{223} - T_{223}\Delta S_{223} = -111 \text{ J/mol}$$

The negative answer (even if the sign of ΔS has been changed, but not if the wrong sign has been used for both ΔH and ΔS) indicates a spontaneous process and tends to rein-

[1] Lesk, A. M., J. CHEM. EDUC., **49**, 660 (1972).
[2] Adamson, Arthur W., "A Textbook of Physical Chemistry," 2nd ed., Academic Press, New York, **1979**, problem 6-6.

force the student's belief that ΔS should be positive. This leads to another misconception.

$\Delta G < 0$ for a *Spontaneous* Process

This is true for *isothermal, constant pressure* changes. This inequality is of such importance that we tend to spend all of our time on it at the expense of conditions for spontaneity in other circumstances.[3] The students quickly adopt it as a general criterion. If a process is not isobaric we can use the Holmholtz Energy, especially if the volume is constant. For non-isothermal cases there is no generally useful relationship between spontaneity and the sign of ΔG or ΔA; ΔS must be used.

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[3] Castellan, Gilbert W., "Physical Chemistry," 3rd ed., Addison-Wesley, Reading, MA, **1983**, p. 207.

[4] Senozan, N. M., J. CHEM. EDUC., **56**, 381 (1979).

[5] Castellan, footnote 3, page 383.

$\Delta H > 0$ for an *Endothermic* Reaction[4]

This is true if *only PV* work is involved. Because textbook examples of non-PV work are almost exclusively found in the electrochemical chapter, students are led to think that the terms exothermic and endothermic are based on the sign of ΔH. In fact, endothermic is a practical description that is properly applied to any reacting system that absorbs heat from the surroundings. If a reaction is carried out irreversibly by direct mixing of the reactants at constant pressure, the heat flow is simply related to the enthalpy change: $Q_P = \Delta H$. Setting up the same reaction in a reversible electrochemical cell will not change ΔH, but the heat flow will be determined by the entropy change: $Q_P = TdS = \Delta H - \Delta G$.[5] Thus, *any* reaction with $\Delta H < 0$ and $\Delta S > 0$ (the always spontaneous case of general chemistry) will be endothermic, that is, will absorb heat, when carried out reversibly in an electrochemical cell.

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