Understanding the Language: Problem Solving and the First Law of Thermodymamics

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Many students, undergraduates and graduates alike, approach physical chemistry with apprehension. The material introduced in physical chemistry is inherently different from other areas of chemistry and requires a greater amount of mathematical expertise (*1*). Looking through various texts (*2, 3*) it is obvious that students are asked to solve problems that involve recognition and use of virial expansions, partial derivatives, and second-order differential equations early in the course.

Many chemistry students are good problem solvers who have algorithmized a variety of different chemistry problems into routine sequential programs (*4, 5*). However, physical chemistry is different enough from other areas of chemistry that many of these algorithms are inadequate for solving physical chemistry problems. For students to build successful algorithms, they must organize the body of mathematical information that they encounter. Fundamentally, the student must learn to translate what he or she reads into mathematical statements and then engage the appropriate algorithm.

Problems associated with the first law of thermodynamics pose difficulty in terms of problem solving for many students of physical chemistry. Words and phrases like "isothermal" ($dT = 0$), "adiabatic" ($dQ = 0$), "constant pressure" ($dp = 0$), and "ideal gas" ($U = U(T), H = H(T), PV = nRT$) all have mathematical meaning that contributes to unraveling and understanding first law problems. If students cannot recognize the connection between these terms and their inherent mathematical meaning, then they are stymied. Once a student can take the given information, describe the problem in operational (mathematical) terms, and then identify the goal, the calculations become much more manageable.

The flow chart helps students decode first law problems that pertain to gases by classifying them according to vocabulary. The mathematical relationships necessary to find heat (Q), work (W), change in energy (ΔU), and change in enthalpy (ΔH) in each case are then summarized. An example illustrates how a student could use this chart.

> If one mole of an ideal gas, $\bar{C}_v = 5/2\,R$, is expanded adiabatically until the temperature drops from 20 °C to 10 °C, calculate Q, W, ΔU, and ΔH. (From ref *2*.)

This problem describes an ideal gas, so the student should use the right side of the chart. Since neither pressure, volume, nor temperature is constant, the student descends to the adiabatic branch. The relationships that would then be helpful are: $Q = 0$, $\Delta U = -W = \int -P_{op}\,dV = n\bar{C}_v\,dT$, $\Delta H = \int n\bar{C}_p\,dT$, and $\bar{C}_p = \bar{C}_v + R$. The student could then perform the following calculations to generate a response:

$$\Delta U = -W = \int_{293}^{283} n\bar{C}_v\,dT = \int_{293}^{283} (1)(5/2\,R)dT = 5/2\,RT\Big|_{293}^{283}$$

$$= 5/2\,R\,(-10\text{ K}) = -208\text{ J}$$

$$\bar{C}_p = 7/2\,R$$

$$\Delta H = \int_{293}^{283} n\bar{C}_p\,dT = \int_{293}^{283} (1)(7/2\,R)\,dT = 7/2\,RT\Big|_{293}^{283}$$

$$= 7/2\,R\,(-10) = -291\text{ J}$$

The answer would be $Q = 0$, $W = 208$ J, $\Delta U = -208$ J, and $\Delta H = -291$ J.

Rather than presenting the chart as an aid to be memorized, it could be developed in class by asking a series of questions in which the students translate thermodynamic terms that are often included in first law problems into operational form (*6*). These mathematical relationships could then be categorized in a fashion that would help students solve first law problems. The students should first identify the type of gas (ideal or other) since this enables the orderly identification of the equation of state and energy and enthalpy relationships. The next separations could be accomplished by holding one variable at a time constant then, finally, considering adiabatic changes. Along the way students have the opportunity to link verbal statements to mathematical relationships. This linkage is vital if the students are to apply their knowledge to first law problems effectively (*7*).

Successfully solving problems pertaining to the first law of thermodynamics begins by understanding what the problem is asking and translating the problem into mathematical statements. This flow chart classifies mathematical relationships into categories that the student can consult for help in solving first law problems. Since knowing how to solve various classes of problems requires considerable practice, it should be emphasized to the students that this chart is not another memorizable nugget of chemistry (*8*). Students should be encouraged to develop algorithms to use in physical chemistry that integrate vocabulary and problem-solving strategies. Using this flow chart may help students build such robust algorithms.

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Ideal Gas

- NO
  - Use equations of state for system
  - **Isothermal**
    - YES
      - $\Delta U = \int \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
      - $\Delta H = \int \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}p$
      - *Reversible*
      - $W = \int p\,\mathrm{d}V$
      - $\Delta U = \int \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
      - $\Delta H = \int \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}p$
    - NO
      - **Constant Pressure**
        - YES
          - $\Delta H = \int n\bar{C}_p\,\mathrm{d}T = Q_p$
          - $\mathrm{d}U = \bar{C}_v \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
        - NO
          - **Adiabatic**
            - YES
              - $Q = 0$
              - $-W = \Delta U = \int -P_{op}\mathrm{d}V = \int n\bar{C}_v\,\mathrm{d}T + \int \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
              - $\mathrm{d}H = \bar{C}_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$
            - NO
              - **Reversible**
                - NO
                  - $\mathrm{d}U = \bar{C}_v \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
                  - $\mathrm{d}H = \bar{C}_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$
                - YES
                  - $W = \int p\,\mathrm{d}V$
                  - $\mathrm{d}U = \bar{C}_v \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$
                  - $\mathrm{d}H = \bar{C}_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p$
- YES
  - $U = U(T)$
  - $H = H(T)$
  - $PV = nRT$
  - **Isothermal**
    - YES
      - $\Delta U = \Delta H = 0$
      - $Q = W$
      - $W = \int P_{op}\mathrm{d}V$
      - *Reversible*
      - $W = nRT \ln (V_f/V_i)$
    - NO
      - **Constant Volume**
        - YES
          - $\mathrm{d}V = 0,\ W = 0$
          - $\Delta U = \int n\bar{C}_v\,\mathrm{d}T = Q$
          - $\Delta H = \int n\bar{C}_p\,\mathrm{d}T$
          - $\bar{C}_p = \bar{C}_v + R$
        - NO
          - **Constant Pressure**
            - YES
              - $\Delta U = \int n\bar{C}_v \mathrm{d}T = Q_p - W$
              - $\Delta H = \int n\bar{C}_p \mathrm{d}T = Q_p$
              - $W = \int P_{op}\,\mathrm{d}V$
              - $\bar{C}_p = \bar{C}_v + R$
            - NO
              - **Adiabatic**
                - NO
                  - $\Delta U = \int n\bar{C}_v \mathrm{d}T$
                  - $\Delta H = \int n\bar{C}_p \mathrm{d}T$
                  - $\bar{C}_p = \bar{C}_v + R$
                - YES
                  - $Q = 0$
                  - $\Delta U = -W = \int -P_{op}\mathrm{d}V = \int n\bar{C}_v \mathrm{d}T$
                  - $\Delta H = \int n\bar{C}_p \mathrm{d}T$
                  - $\bar{C}_p = \bar{C}_v + R$
                  - *Reversible*
                  - $\int -P_{op}\,\mathrm{d}V = \int -\frac{nRT}{V}\mathrm{d}V = \int n\bar{C}_v \mathrm{d}T$
                  - Upon integration
                  - $-R \ln (V_f/V_i) = \bar{C}_v \ln (T_f/T_i)$

Flow Chart for solving first-law problems. Definitions:

$\bar{C}_p$ = Molar heat capacity at constant pressure
$\bar{C}_v$ = Molar heat capacity at constant pressure
Q = Heat (Positive if a mass in the surroundings has cooled)
W = Work (Positive if a weight in the surroundings has been lifted)

The First Law (Chapter 2)