

**Big idea #1:** For a set of quantized energy states, Boltzmann factors determine the occupation probabilities of each state, which in turn dictate macroscopic properties.

**Learning target:** The Boltzmann factor ( $e^{-\varepsilon/k_B T}$ ) is proportional to the probability that a quantized energy state will be occupied at a given temperature. The partition function ( $q$ ) is a sum of all Boltzmann factors of a system.

**Sample success criteria:**

- Qualitatively describe how raising the temperature or increasing the spacing between states changes the probability that excited states will be populated.
- For a given set of states at a given temperature, calculate the partition function and the probabilities that each state will be occupied.

**Learning target:** The inherent distinguishability or indistinguishability of the particles affects how multi-particle states are counted, and consequently affects their occupation probabilities.

**Sample success criteria:**

- For a system with a small number of states and particles, write the exact partition functions ( $Q$ ) for distinguishable particles, indistinguishable bosons, and indistinguishable fermions. In each case, calculate the probability that each multi-particle state will be occupied.
- For a system with many unoccupied states, explain how and why to make a reasonable approximation for the partition function of bosons or fermions.

**Learning target:** Macroscopic properties, such as the average energy and heat capacity of a system, can be expressed in terms of the partition function.

**Sample success criteria:**

- Given the expression for average energy in terms of partition function (which you do not have to memorize), calculate the average energy and heat capacity of a system.

**Learning target:** Diatomic and polyatomic molecules can be viewed as having independent sets of translational, vibrational, rotational, and electronic energy states. The partition functions of such molecules, and therefore their macroscopic properties, can be estimated based on quantum model systems.

**Sample success criteria:**

- Rank the components of a molecule's partition function (translational, vibrational, rotational, electronic) from smallest to largest.
- State which quantum model system is used to approximate each component of a molecule's energy. Understand where the derivations of each component of the energy and heat capacity are coming from (though you don't need to remember every step).
- Explain in words the meaning of a diatomic molecule's vibrational temperature ( $\Theta_{\text{vib}}$ ) and rotational temperature ( $\Theta_{\text{rot}}$ ).
- Given values of  $\Theta_{\text{vib}}$  or  $\Theta_{\text{rot}}$ , calculate the fractional population of each vibrational or rotational energy level at a given temperature. Given two diatomic molecules, predict which has a larger  $\Theta_{\text{vib}}$  or  $\Theta_{\text{rot}}$ .
- Predict the molar constant-volume heat capacities of diatomic and polyatomic molecules using simple assumptions (e.g., a temperature too low to excite vibrational modes, or high enough to excite all vibrational modes).

**Learning target:** The macroscopic behavior of ideal gases is governed by the ideal gas law ( $PV = nRT$ ), which follows from statistical mechanics. Real gases are influenced by the size of and forces among atoms and molecules.

**Sample success criteria:**

- Use the ideal gas law to calculate basic relationships among the macroscopic properties of an ideal gas (e.g., pressure, volume, temperature, molar mass, and density).
- Recognize that temperature is proportional to the kinetic energy of an ideal gas, and use that fact to compare the average speeds of different gases.
- Explain the intuitive meaning of the empirical parameters  $a$  and  $b$  in the van der Waals equation, which relates the macroscopic properties of a real gas.
- Understand how supercriticality arises from the size and attractive forces of a real gas. Recognize the differences among a gas, a liquid, and supercritical fluid in a pressure-volume diagram.

**Big idea #2:** Energy in macroscopic systems is transferred in the forms of work and heat, and the energy of the universe is conserved.

**Learning target:** Pressure-volume work ( $w = -\int P_{\text{external}}dV$ ) is done when a gas expands or is compressed.

**Sample success criteria:**

- For a path through a pressure-volume diagram or a described process, identify the sign of  $w$ , and if given enough information, calculate the value of  $w$ .
- For different paths through a pressure-volume diagram, compare the values of  $w$ , recognizing that the absolute value of  $w$  is the area under each curve.

**Learning target:** Heat is the spontaneous transfer of energy from a hotter object to a colder object.

**Sample success criteria:**

- When an ideal gas expands at constant temperature, deduce whether heat is transferred to or from the gas, and explain how you know that.

**Learning target:** The first law of thermodynamics ( $\Delta U = q + w$ ) states that the energy of the universe is conserved, and that energy can be transferred to or from a system as heat or work.

**Sample success criteria:**

- Calculate  $\Delta U$ ,  $q$ , and  $w$  for the isothermal compression of an ideal gas from volume  $V_1$  to  $V_2$  at temperature  $T$ .
- Calculate  $\Delta U$ ,  $q$ , and  $w$  for a given straight-line path through a pressure-volume diagram.

**Learning target:** Certain idealized conditions (e.g., isothermal, adiabatic, or constant-volume) make it easier for us to know one or more of the quantities in the first law of thermodynamics.

**Sample success criteria:**

- For given pathways and circuits through a pressure-volume diagram, state the signs (+, -, or 0) of  $\Delta U$ ,  $q$ , and  $w$ .
- Calculate the change in temperature during the reversible adiabatic compression of an ideal gas starting at temperature  $T_1$  from volume  $V_1$  to  $V_2$ .

**Learning target:** State functions depend only on a system's conditions at a given time, and not on how the system got there.

**Sample success criteria:**

- Determine which of these are state functions: internal energy, work, heat, temperature, pressure, volume.

**Learning target:** Calorimetry measures the heat transfer associated with a chemical or physical process. Any heat released in the process is taken in by the calorimeter, and vice versa.

**Sample success criteria:**

- Given the initial temperatures and heat capacities of two substances in thermal contact, calculate the equilibrium temperature they eventually reach.

**Learning target:** While heat is path-dependent in general, heat transfer in certain conditions is equal to the change in a state function. Heat transfer at constant volume is equal to the change in internal energy ( $U$ ), and heat transfer at constant pressure is equal to the change in enthalpy ( $H = U + PV$ ).

**Sample success criteria:**

- Understand the distinction between constant-volume and constant-pressure heat capacity, and explain why constant-pressure heat capacity is always the larger of the two.
- Explain which type of calorimeter, bomb or coffee cup, is more appropriate for measuring changes in internal energy, and which is more appropriate for measuring changes in enthalpy.
- Given  $\Delta H$  of a reaction, the amount of reactants, and the heat capacity of the calorimeter, calculate the temperature change of the calorimeter.

**Learning target:** Because enthalpy is a state function, enthalpies of reaction are additive and can be usefully tabulated in textbooks.

**Sample success criteria:**

- Given  $\Delta H$  for relevant reactions, use Hess's law to calculate  $\Delta H$  for a reaction of interest.
- Given the relevant standard enthalpies of formation, calculate  $\Delta H$  for a reaction of interest.

**Big idea #3:** Entropy quantifies microscopic disorder, which tends to spontaneously increase.

**Learning target:** A given outcome of an event (chemical, physical, or otherwise) is more likely to occur if there are more “microstates” leading to it. This idea is quantified by the Boltzmann entropy formula ( $S = k_B \ln W$ ).

**Sample success criteria:**

- Explain why, even though one coin flip is equally likely to land heads or tails, the outcomes of 10 coins flips are more likely to be 6 heads/4 tails than 7 heads/3 tails. Calculate the probability of each of these outcomes.

**Learning target:** Entropy, the change in which is defined by  $dS = \frac{\delta q_{\text{rev}}}{T}$ , is a state function quantifying disorder.

**Sample success criteria:**

- Calculate the change in entropy during a given isothermal or adiabatic process.
- For a path through a pressure-volume diagram that ends at the same point where it started, explain why the change in entropy must be zero.

**Learning target:** The second law of thermodynamics states that the entropy of an isolated system (e.g., the universe) spontaneously increases over time.

**Sample success criteria:**

- Given the changes in entropy of a system and its surroundings, determine whether a process is spontaneous, reversible, or impossible.
- For a simple process like the reversible, isothermal compression of ideal gas in a piston, find the changes entropy of the system and surroundings.

**Learning target:** Unlike internal energy or enthalpy, entropy can be quantified in an absolute sense. The third law of thermodynamics states that a perfect crystal at absolute zero temperature has zero entropy.

**Sample success criteria:**

- Given the temperature-dependent heat capacity of a substance and its  $\Delta H$  for phase transitions, calculate the change in entropy as that substance undergoes temperature and phase changes.

**Learning target:** Absolute entropy can be seen as disorder in the accessible energy states of a substance. Using this reasoning, it is possible to rank the absolute entropies of different substances.

**Sample success criteria:**

- Given a pair of substances that differ in some way (e.g., temperature, volume, molar mass, rigidity of ring structure), determine which has more entropy and explain why.

**Learning target:** Because entropy is a state function, absolute entropies are tabulated, and the change in entropy of a reaction can be calculated.

**Sample success criteria:**

- Estimate the sign and magnitude of  $\Delta S$  of a reaction based in the change in number of moles of gas.
- Given the relevant standard entropies, calculate  $\Delta S$  for a reaction of interest.

**Big idea #4:** The spontaneity of a chemical or physical process is driven by both decreasing energy and increasing entropy.

**Learning target:** Helmholtz and Gibbs energies are state functions designed to quantify the spontaneity of processes in constant-volume and constant-pressure conditions, respectively.

**Sample success criteria:**

- Given the changes in energy ( $\Delta U$  or  $\Delta H$ ) and entropy ( $\Delta S$ ) associated with chemical or physical processes, identify the temperature ranges in which those processes occur spontaneously or reversibly.

In CHEM 463, this big idea will be explored further in the context of phase diagrams and equilibrium.