1. If the gases in these two containers are at different pressures, when the pins holding the pistons are released, the pistons move one way or the other until the two pressures are the same. The two systems are then in mechanical equilibrium. If the pressures are the same to begin with, there is no movement of the pistons when the pins are withdrawn, for the two systems are already in mechanical equilibrium.

2. A representation of the zeroth law involving (top left) three systems that can be brought into thermal contact. If A is found to be in thermal equilibrium with B (top right), and B is in thermal equilibrium with C (bottom left), then we can be confident that C will be in thermal equilibrium with A if they are brought into contact (bottom right).
3. Three common temperature scales showing the relations between them. The vertical dotted line on the left shows the lowest achievable temperature; the two dotted lines on the right show the normal freezing and boiling points of water.

4. The Boltzmann distribution is an exponentially decaying function of the energy. As the temperature is increased, the populations migrate from lower energy levels to higher energy levels. At absolute zero, only the lowest state is occupied; at infinite temperature, all states are equally populated.
5. The Maxwell–Boltzmann distribution of molecular speeds for molecules of various mass and at different temperatures. Note that light molecules have higher average speeds than heavy molecules. The distribution has consequences for the composition of planetary atmospheres, as light molecules (such as hydrogen and helium) may be able to escape into space.

6. The observation that different ways of doing work on a system and thereby changing its state between fixed endpoints required the same amount of work is analogous to different paths on a mountain resulting in the same change of altitude leads to the recognition of the existence of a property called the internal energy.
7. When a system is adiabatic (left), a given change of state is brought about by doing a certain amount of work. When the same system undergoes the same change of state in a non-adiabatic container (right), more work has to be done. The difference is equal to the energy lost as heat.

8. The molecular distinction between the transfer of energy as work (left) and heat (right). Doing work results in the uniform motion of atoms in the surroundings; heating stimulates their disorderly motion.
9. The Kelvin (left) and Clausius (right) observations are, respectively, that a cold sink is essential to the operation of a heat engine and that heat does not flow spontaneously from a cooler to a hotter body.

10. The equivalence of the Kelvin and Clausius statements. The diagram on the left depicts the fact that the failure of the Kelvin statement implies the failure of the Clausius statement. The diagram on the right depicts the fact that the failure of the Clausius statement implies the failure of the Kelvin statement.
11. An engine like that denied by Kelvin's statement (left) implies a reduction in entropy and is not viable. On the right is shown the consequence of providing a cold sink and discarding some heat into it. The increase in entropy of the sink may outweigh the reduction of entropy of the source, and overall there is an increase in entropy. Such an engine is viable.

12. The increase in entropy of a collection of particles in an expanding box-like region arises from the fact that as the box expands, the allowed energies come closer together. Provided the temperature remains the same, the Boltzmann distribution spans more energy levels, so the chance of choosing a molecule from one level in a blind selection decreases. That is, the disorder and the entropy increase as the gas occupies a greater volume.
13. The residual entropy of water, reflecting its 'degeneracy' at $T = 0$, arises from the variation in the locations of hydrogen atoms (the small white spheres) between oxygen atoms (the shaded spheres). Although each oxygen atom is closely attached to two hydrogen atoms and makes a more distant link to a hydrogen atom of each of two neighbouring water molecules, there is some freedom in the choice of which links are close and which are distant. Two of the many arrangements are shown here.

14. The processes involved in a refrigerator and a heat pump. In a refrigerator (left), the entropy of the warm surroundings is increased by at least the amount by which the entropy of the system (the interior of the refrigerator) is decreased; this increase is achieved by adding to the flow of energy by doing work. In a heat pump (right), the same net increase in entropy is achieved, but in this case the interest lies in the energy supplied to the interior of the house.
15. On the left a process occurs in a system that causes a change in internal energy $\Delta U$ and a decrease in entropy. Energy must be lost as heat to the surroundings in order to generate a compensating entropy there, so less than $\Delta U$ can be released as work. On the right, a process occurs with an increase in entropy, and heat can flow in to the system yet still correspond to an increase in total entropy; as a result, more than $\Delta U$ can be released as work.

16. The decrease in Gibbs energy with increasing temperature for three phases of a substance. The most stable phase corresponds to the lowest Gibbs energy; thus the solid is most stable at low temperatures, then the liquid, and finally the gas (vapour). If the gas line falls more steeply, it might intersect the solid line before the liquid line does, in which case the liquid is never the stable phase and the solid sublimes directly to a vapour.
17. A process that corresponds to a large increase in total energy (represented here by an increase in disorder on the left) can drive a process in which order emerges from disorder (on the right). This is analogous to a falling heavy weight being able to raise a lighter weight.

18. A molecular model of adenosine triphosphate (ATP). Some of the phosphorus (P) and oxygen (O) atoms are marked. Energy is released when the terminal phosphate group is severed at the location shown by the line. The resulting ADP molecule must be ‘recharged’ with a new phosphate group: that recharging is achieved by the reactions involved in digestion and metabolism of food.
19. The variation of the Gibbs energy of a reaction mixture as it changes from pure reactants to pure products. In each case, the equilibrium composition, which shows no further net tendency to change, occurs at the minimum of the curve.

20. The process of adiabatic demagnetization for reaching low temperatures. The arrows depict the spin alignment of the electrons in the sample. The first step (M) is isothermal magnetization, which increases the alignment of the spins, the second step (D) is adiabatic demagnetization, which preserves the entropy and therefore corresponds to a lowering of temperature. If the two curves did not meet at \( T = 0 \), it would be possible to lower the temperature to zero (as shown on the left). That a finite sequence of cycles does not bring the temperature to zero (as shown on the right) implies that the curves meet at \( T = 0 \).
21. The variation of (left) the internal energy and (right) the entropy for a two-level system. The expressions for these two properties can be calculated for negative temperatures, as shown on the left of each illustration. Just above $T = 0$ all the molecules are in the ground state; just below $T = 0$ they are all in the upper state. As the temperature becomes infinite in either direction, the populations become equal.

22. The same system as in Figure 21 but plotted against $\beta$ instead of $T$. The internal energy varies smoothly across the range.