Phase Changes and Refrigeration: Thermochemistry of Heat Engines

Thermochemistry Experiment

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Key Concepts

- Heat Engines
- Reverse Heat Engines (*e.g.*, Refrigerators)
- Phases of Matter
    - Solid
    - Liquid
    - Gas
- Phase Transitions
    - Fusion/ Freezing
    - Vaporization/ Condensation
    - Sublimation/ Deposition
- Breaking or Formation of Intermolecular Attractions in Phase Transitions
- Change in Enthalpy (ΔH) of Phase Transitions
- Refrigeration Cycle

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- *Bands, Bonds, and Doping: How Do LEDs Work?*
- *Gas Laws Save Lives: The Chemistry Behind Air Bags*

Introduction: Heat Engines and Refrigeration

Refrigeration has allowed for great advances in our ability to store food and other substances safely for long periods of time. The same technology used to run refrigerators is also used in air conditioners. How does this technology work to produce cool air when the external conditions are hot? As we shall see, refrigerators (and air conditioners) rely on the thermodynamic application known as the heat engine, as well as the molecular properties of the substance contained in the coils of the refrigerator.

One of the most important practical applications of the principles of thermodynamics is the heat engine (Figure 1). In the heat engine, heat is absorbed from a "**working substance**" at high temperature and partially converted to work. Heat engines are never 100% efficient, because the remaining heat (*i.e.*, the heat is not converted to work) is released to the surroundings, which are at a lower temperature. The steam engines used to power early trains and electric generators are heat engines in which water is the working substance. In a reverse heat engine (Figure 2), the opposite effect occurs. Work is converted to heat, which is released.

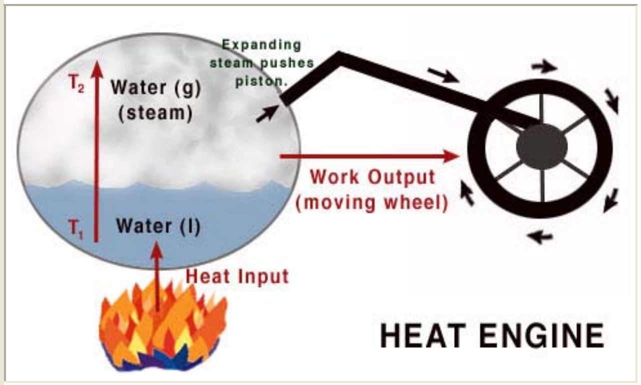


Figure 1

In a heat engine, an input of heat causes an increase in the temperature of the working substance, allowing the working substance to perform work. In this schematic diagram, the working substance is water. At high temperature, gaseous water (steam) pushes a piston, which causes a wheel to turn. This is the essential mechanism by which steam-powered trains operate.

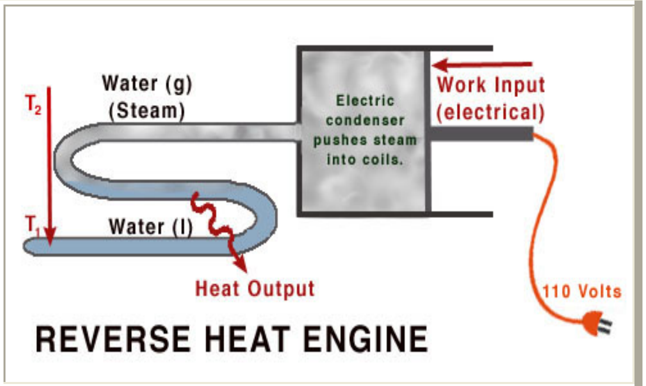


Figure 2

In a reverse heat engine, a work input is converted to a heat output. In this case, the work (generated by electricity) condenses gaseous water (steam) and pushes it into a heat-exchange coil. In the coil, the temperature of the water lowers as it liquefies, releasing heat to the environment.

In 1851, the Florida physician John Gorrie was granted the first U.S. Patent for a refrigeration machine, which uses a reverse heat engine (Figure 2) as the first step in its operation. Gorrie, convinced that the cure for malaria was cold because outbreaks were terminated in the winter, sought to develop a machine that could make ice and cool a patient's room in the hot Florida summer. In Dr. Gorrie's refrigerator, air was compressed using a pump, which caused the temperature of the air to increase (exchanging work for heat). Running this compressed air through pipes in a cold-water bath released the heat into the water. The air was then allowed to expand again to atmospheric pressure, but because it had lost heat to the water, the temperature of the air was lower than before and could be used to cool the room.

Modern refrigerators operate by the same reverse-heat-engine principle of converting work to heat, but use substances other than air. The working substance in a modern refrigerators is called the coolant; the coolant changes from gas to liquid as it goes from higher to lower temperature. This change from gas to liquid is a phase transition, and the energy released upon this transition is mainly dependent on the intermolecular interactions of the substance. Hence, to understand the refrigeration cycle used in modern refrigerators, it is necessary to first discuss phase transitions.

Phases and Phase Transitions

Matter mainly exists in three different phases (physical states): solid, liquid, and gas. A phase is a form of matter that is uniform in chemical composition and physical properties. As shown in Figure 3, a substance in the solid phase has a definite shape and volume; a substance in the liquid phase has no definite shape, but has a definite volume; a substance in the gas phase has no definite shape or volume, but has a shape and volume determined by the shape and size of the container.

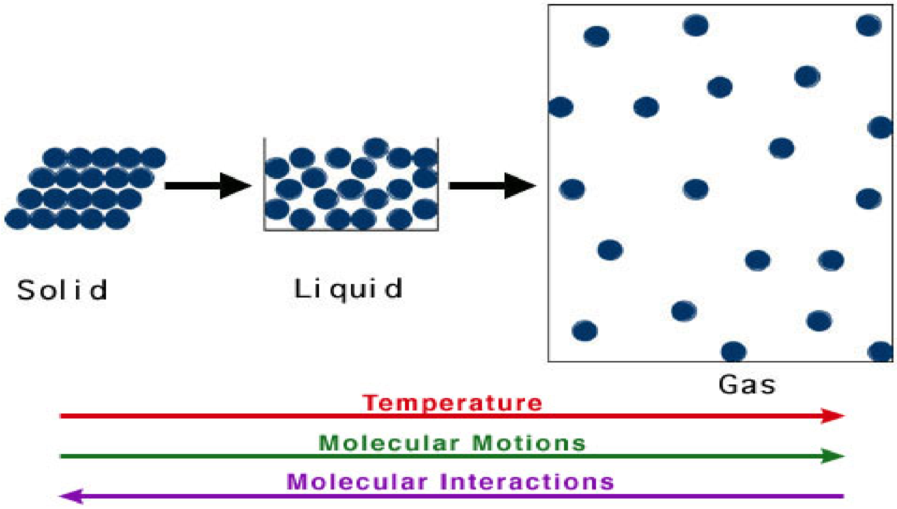


Figure 3

This schematic diagram shows the differences in physical properties and particle arrangement between a substance in the solid, liquid, and gas phases. In a solid, the particles are packed in a rigid configuration, giving the substance a definite shape and size. In a liquid, the particles are close together but may move with respect to one another, giving the substance a definite volume but a fluid shape. In a gas, the particles may occupy the entire volume of the container, so that their shape and volume are both defined by the container.

Molecular (Microscopic) View

One of the major differences in the three phases illustrated in Figure 3 is the number of intermolecular interactions they contain. The particles in a solid interact with all of their nearest neighbors, the particles in a liquid interact with only some of the nearby particles, and the particles in a gas have almost no interaction with one another. By breaking or forming intermolecular interactions, a substance can change from one phase to another. For example, gas molecules condense to form liquids because of the presence of attractive intermolecular forces. The stronger the attractive forces, the greater the stability of the liquid (which leads to a higher boiling point temperature). A change in the physical state of matter is called a phase transition. The names of the phase transitions between solid, liquid, and gas are shown in Figure 4.

Phase transitions are similar to chemical reactions as they each have an associated enthalpy change. While a chemical reaction involves the breaking and forming of bonds within molecules, phase transitions involve the breaking or forming of intermolecular attractive forces. Phase transitions involving the *breaking* of intermolecular attractions (such as fusion, vaporization, and sublimation) require an input of energy to overcome the attractive forces between the particles of the substance. Phase transitions involving the *formation* of intermolecular attractions (such as freezing, condensation, and deposition) release energy as the particles adopt a lower-energy conformation. The strength of the intermolecular attractions between molecules, and therefore the amount of energy required to overcome these attractive forces (as well as the amount of energy released when the attractions are formed) depends on the molecular properties of the substance. Generally, the more polar a molecule is, the stronger the attractive forces between molecules are. Hence, more polar molecules typically require more energy to overcome the intermolecular attractions, and release more energy by forming intermolecular attractions.

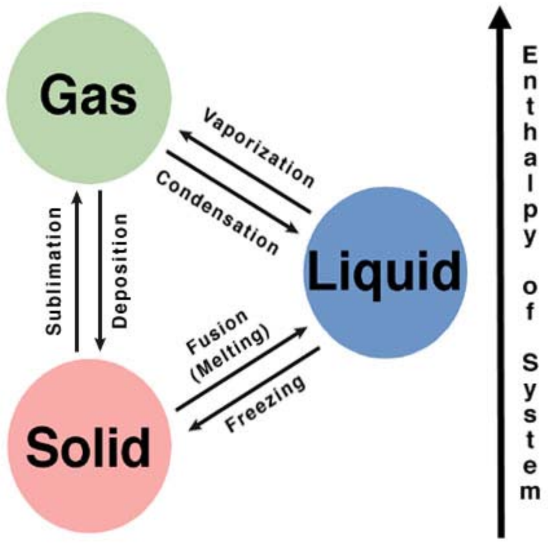


Figure 4

This diagram shows the names of the phase transitions between solids, liquids, and gases. The arrow to the right of the diagram demonstrates that these three phases have different enthalpies: gas has the highest enthalpy, liquid has an intermediate enthalpy, and solid has the lowest enthalpy.

Phase Transition	Change of Enthalpy
Fusion (Melting) (solid to liquid)	$\Delta H > 0$; enthalpy increases (endothermic process)
Vaporization (liquid to gas)	$\Delta H > 0$; enthalpy increases (endothermic process)
Sublimation (solid to gas)	$\Delta H > 0$; enthalpy increases (endothermic process)
Freezing (liquid to solid)	$\Delta H < 0$; enthalpy decreases (exothermic process)
Condensation (gas to liquid)	$\Delta H < 0$; enthalpy decreases (exothermic process)
Deposition (gas to solid)	$\Delta H < 0$; enthalpy decreases (exothermic process)

Table 1

This table shows the sign of the enthalpy change for each of the phase transitions described above. Recall that endothermic processes have a positive enthalpy change, and exothermic processes have a negative enthalpy change.

Thermodynamic (Macroscopic) View

In addition to the microscopic view presented above, we can describe phase transitions in terms of macroscopic, thermodynamic properties. It is important to bear in mind that the microscopic and macroscopic views are interdependent; *i.e.*, the thermodynamic properties, such as enthalpy and temperature, of a substance are dependent on the molecular behavior of the substance.

Phase transitions are accompanied by changes in enthalpy and entropy. In this tutorial, we will concern ourselves mainly with changes in enthalpy. The energy change involved in breaking or forming intermolecular attractions is primarily supplied or released in the form of heat. Adding heat causes intermolecular attractions to be broken. How does this occur? Heat is a transfer of energy to molecules, causing the molecules to increase their motion as described by the kinetic theory of gases and thereby weakening the intermolecular forces holding the molecules in place. Likewise, when molecules lose heat, intermolecular attractions are strengthened; as heat is lost, the molecules move slower and therefore can interact more with other nearby molecules.

Because phase changes generally occur at constant pressure (*i.e.*, in a reaction vessel open to the atmosphere), the heat can be described by a change in enthalpy ($\Delta H = q_p$). For phase transitions involving the breaking of intermolecular attractions, heat is added and ΔH is positive, the system is going from a lower-enthalpy phase to a higher-enthalpy phase (an endothermic process). Hence, fusion, vaporization, and sublimation are all endothermic phase transitions. For phase transitions involving the forming of intermolecular attractions, heat is released and ΔH is negative, because the system is going from a higher-enthalpy phase to a lower-enthalpy phase (an exothermic process). Hence, freezing, condensation, and deposition are all exothermic phase transitions. The enthalpy change for each of the phase-transition processes in Figure 4 is shown in Table 1 above.

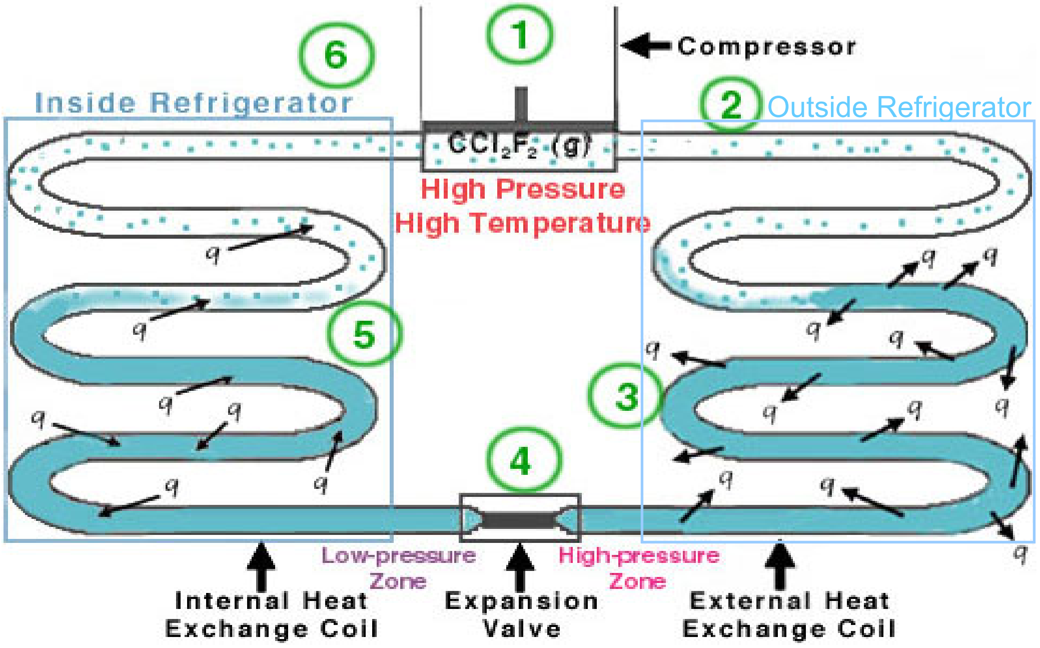
The enthalpy change of phase transitions can also be used to explain differences in melting points and boiling points of substances. At a given pressure, a substance has a characteristic range of temperatures at which it undergoes phase transitions; for example, melting point is the temperature at which a substance changes from solid phase to liquid phase and boiling point is the temperature at which a substance changes from liquid phase to gaseous phase. In general, the greater the enthalpy change for a phase transition, the higher the temperature at which the substance undergoes the phase transition**.** For example, liquids with strong intermolecular attractions require more heat to vaporize than liquids with weak intermolecular attractions; therefore, the boiling point (vaporization point) for these liquids will be higher than for the liquids with weaker intermolecular attractions.

Refrigeration

Now, we shall use our understanding of heat engines and phase transitions to explain how refrigerators work. The enthalpy changes associated with phase transitions may be used by a heat engine (Figure 1) to do work and to transfer heat between the substance undergoing a phase transition and its surrounding environment. In a heat engine, a "working substance" absorbs heat at a high temperature and converts part of this heat to work. In a secondary process, the rest of the heat is released to the surroundings at a lower temperature, because the heat engine is not 100% efficient.

As shown in Figure 2, a refrigerator can be thought of as a heat engine in reverse. The cooling effect in a refrigerator is achieved by a cycle of condensation and vaporization of the coolant, which usually is the nontoxic compound CCl_2F_2 (Freon-12). A refrigerator contains an electrically-powered compressor that does work on Freon gas. Coils outside the refrigerator allow Freon to release heat when it condenses, and coils inside the refrigerator allow Freon to absorb heat as it vaporizes. Figure 5 shows the phase transitions of Freon and their associated heat-exchange events that occur during the refrigeration cycle.

Figure 6 Major steps in the refrigeration cycle



Click on the pink button to view a QuickTime movie showing an animation of the refrigeration cycle. Click the blue button to download QuickTime to view the movie.

View the Movie

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1. Outside of the refrigerator, the electrically-run compressor does work on the Freon gas, increasing the pressure of the gas. As the pressure of the gas increases, so does its temperature (as predicted by the ideal-gas law).
2. This high-pressure, high-temperature gas enters the coil on the outside of the refrigerator.
3. Heat (q) flows from the high-temperature gas to the lower-temperature air of the room surrounding the coil. This heat loss causes the high-pressure gas to condense to liquid, as motion of the Freon molecules decreases and intermolecular attractions increases. Hence, the work done on the gas by the compressor (causing an exothermic phase transition in the gas) is converted to heat given off in the air in the room outside the refrigerator.
4. The liquid Freon in the external coil passes through an expansion valve into a coil inside the insulated compartment of the refrigerator. Now, the liquid is at a low pressure (as a result of the expansion) and is lower in temperature (cooler) than the air inside the refrigerator.
5. Since heat is transferred from areas of greater temperature to areas of lower temperature, heat is absorbed (from inside the refrigerator) by liquid Freon, causing the temperature inside the refrigerator to be reduced. The absorbed heat begins to break the intermolecular attractions of the liquid Freon, allowing the endothermic vaporization process to occur.
6. When all of the Freon changes to gas, the cycle can start over.

The cycle described above does not run continuously, but rather is controlled by a thermostat. When the temperature inside the refrigerator rises above the set temperature, the thermostat starts the compressor. Once the refrigerator has been cooled below the set temperature, the compressor is turned off. This control mechanism allows the refrigerator to conserve electricity by only running as much as is necessary to keep the refrigerator at the desired temperature.

Summary

Refrigerators are essentially heat engines working in reverse. Whereas a heat engine converts heat to work, reverse heat engines convert work to heat. In the refrigerator, the heat that is generated is transferred to the outside of the refrigerator. To cool the refrigerator, a "working substance", or "coolant", such as Freon is required. The refrigerator works by using a cycle of compression and expansion on the Freon. Work is done on the Freon by a compressor, and the Freon releases heat to the air outside of the refrigerator (as it undergoes the exothermic condensation from a gas to a liquid). To regenerate the gaseous Freon for compression, the Freon passes through an internal coil, where it undergoes the endothermic vaporization from the liquid phase to the gaseous phase. This endothermic process causes the Freon to absorb heat from the air inside the refrigerator, cooling the refrigerator.

Additional Links:

- For more explanation about how refrigerators work, see this site from "How Stuff Works," by Marshall Brian.
- This site has an essay on thermodynamics by Isaac Asimov.

References:

Brown, Lemay, and Bursten. *Chemistry: The Central Science*, 7th ed., p. 395-98.

Petrucci and Harwood. *General Chemistry*, 7th ed., p. 435, 699-701, 714-15.

Acknowledgements:

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