Mars Terraforming Examples
Chapter 6 (thermodynamic systems, enthalpy, specific heat, calorimetry, Hess' Law, heat of formation)

Thermodynamic Systems
Terraforming Mars will require many things, but most of all, it requires energy. Nuclear power plants brought from Earth will provide some energy but most energy will come from the Sun. Plants will absorb light in order to convert CO_2 to O_2. Orbiting mirrors will collect solar energy and focus the sunlight onto a small area in order to melt frozen CO_2 and ice. Once water and a thicker atmosphere appear on Mars, clouds will form and these will reflect some of the sunlight back into space. Would all this make Mars a closed open or isolated system?
(Mars is a closed system. Energy can enter and leave but not mass. On the other hand, if the materials brought from Earth to Mars are considered, Mars would be an open system since mass is entering the system.)

Enthalpy
1. Consider the following processes.
Greenhouse gases absorb sunlight and prevent the heat from escaping back into space. This will cause the temperature on Mars to change from -60 °C to 5 °C. If all of Mars is the system, is this process endothermic or exothermic? (endothermic)
The factory that creates the greenhouse gases requires power from a small nuclear reactor. Is the process of making the greenhouse gases endothermic or exothermic? (endothermic)
Rocket propellants such as CH_4/O_2 and H_2/O_2 mixtures react and produce enough energy to move spaceships away from Earth and towards Mars. Is the burning of propellant an endothermic or exothermic reaction? (exothermic)

2. The following reaction might be used to generate the greenhouse gases needed to warm Mars:
$CH_{4\,g} + 2\,SO_3 + 8\,F_2 \rightarrow CF_{4\,g} + 2\,SF_{6\,g} + 2\,H_{2\,g} + 3\,O_{2\,g}$
$\Delta H_{rxn} = -2485$ kJ
Endothermic or exothermic? (exothermic)
What is ΔH_{rxn} per mole of $F_{2\,g}$ used? (-310.6 kJ/mol F_2)

Earlier, we said that the production of greenhouse gases would require power from a small nuclear reactor because the production of gases was an endothermic process. So why is the above reaction exothermic?
CO_2 and SO_3 can be found on Mars but we haven't considered how we will make $F_{2\,g}$ and $CH_{4\,g}$. Fluorine gas does not exist in the Martian atmosphere and it must be produced from CaF_2 rocks. The reaction is:
$CaF_{2\,s} \rightarrow Ca_{\,s} + F_{2\,g}$ $\quad\quad \Delta H_{rxn} = 1228$ kJ
Is this reaction endothermic or exothermic? (endothermic)
How much energy is required to make the 8 moles of $F_{2\,g}$ needed for the production of SF_6 and CF_4?
(8 x 1228 = 9824 kJ)

CH_4 will have to be made also. Starting with $CO_{2\,g}$ in the atmosphere and $H_{2\,g}$ brought from Earth or produced in other reactions, the production of methane occurs by the reaction:

$CO_{2\,g} + 2\ H_{2\,g} \rightarrow CH_{4\,g} + O_{2\,g}$ $\Delta H_{rxn} = 318.5$ kJ

Is this reaction endothermic or exothermic? (endothermic)

Which is process requires less energy, production of a mole of F_2 or CH_4? (CH_4)

Even though production of greenhouse gases will require lots of energy, there is a silver lining to this whole process. The reactions make O_2 and Ca metal, which can react in an exothermic reaction:

$2\ Ca_s + O_2 \rightarrow 2\ CaO$ $\Delta H_{rxn} = 1270$ kJ

If 4 moles of oxygen gas and 8 moles of Ca metal are combined, how much energy is released when they react?

(5080 kJ)

<u>Specific Heat</u>

SF_6 and CH_4 are greenhouse gases that will be produced on Mars to help raise the temperature. An insulated reactor will contain F_2, CO_2 and SO_3 gases heated to 40 °C. The reaction that will take place is:

$CH_{4\,g} + 2\ SO_3 + 8\ F_2 \rightarrow CF_{4\,g} + 2\ SF_{6\,g} + 2\ H_{2\,g} + 3\ O_{2\,g}$

Since the outside temperature on Mars will be -60 °C initially, energy must be supplied to heat the reactants to 40 °C. If stoichiometric amounts of reactants are placed in the reaction chamber, how much energy is needed to warm the reactants from -60 °C to 40 °C? The specific heat of each material is provided below. Assume that the reaction chamber is well insulated and so there is no heat loss.

$s(CH_{4\,g}) = 9.82$ J/(g °C)

$s(SO_{3\,g}) = 0.634$ J/(g °C)

$s(F_{2\,g}) = 0.824$ J/(g °C)

(509 J/°C for combined reactants, 50.9 kJ for 100 °C temperature change.)

<u>Calorimetry</u>

1. One significant difference between Earth and Mars is that there are no fossil fuels on Mars. Space vehicles that return to Earth from Mars will have to be very fuel-efficient. As a scientist at NASA, you are asked to determine the enthalpy for the combustion of each of the following fuels using a bomb calorimeter. All the fuels will react with excess oxygen at 278 K.

The calorimeter contains 1000 g of H_2O and has a calorimeter constant of 11.3 kJ/°C. Three experiments were performed and the temperature changes noted:

material	ΔT (°C)	reaction
1.15 g $H_{2\,g}$	14.3	$H_{2\,g} + {}^1/_2\ O_{2\,g} \rightarrow H_2O_L$
1.50 g $CH_{4\,g}$	7.3	$CH_{4\,g} + 2\ O_{2\,g} \rightarrow CO_{2\,g} + 2\ H_2O_L$

Determine ΔH_{rxn}/mol fuel (either $CH_{4\,g}$ or $H_{2\,g}$).
(For the combustion of $H_{2\,g}$, q = - 161.6 kJ for 1.15 g or - 283.3 kJ/mol. Since Δn = - 1.5/mol H_2 and $\Delta H = q + RT\Delta n$, ΔH = - 286.8 kJ/mol.
For the combustion of $CH_{4\,g}$, q = - 82.5 kJ for 1.50 g or - 879.9 kJ/mol, Δn = -2/mol CH_4, ΔH = - 884.5 kJ/mol.)

2. As plants convert CO_2 to O_2, some of the oxygen will react with minerals and oxidize them. For instance, both FeO and Fe_2O_3 are found on Mars. FeO can react with O_2 to make Fe_2O_3 in the following reaction:
$4\ FeO_s + O_{2\,g} \rightarrow 2\ Fe_2O_{3\,s}$ $\quad \Delta H_{rxn}$ = - 564 kJ
Since O_2 is a gas, this reaction will only occur on the surface of a FeO rock.

If a 5.05 kg chunk of FeO is exposed to O_2, what will be the temperature change of the rock due to the oxidation of 20.07 g of FeO on the surface? Since most of the rock remains FeO, assume that s_{soln} = s(FeO) = 1.40 J/(g °C). Assume that all the energy released from the oxidation reaction is absorbed by the rock.
(ΔH_{rxn} = - 564 kJ for 4 mol FeO = 141 kJ/mol FeO = 1.96 kJ/g FeO. For 20.7 g FeO, ΔH_{rxn} = 40.6 kJ. ΔT = 5.74 K.)

<u>Hess' Law and Heat of Formations</u>
The production of greenhouse gases (CF_4 and SF_6) on Mars may require the following reactions:
$CO_{2\,g} + 2\ H_{2\,g} \rightarrow CH_{4\,g} + O_{2\,g}$ $\quad \Delta H_{rxn}$ = 318.5 kJ
$CaF_{2\,s} \rightarrow Ca_s + F_{2\,g}$ $\quad \Delta H_{rxn}$ = 1228 kJ
$CH_{4\,g} + 2\ SO_3 + 8\ F_2 \rightarrow CF_{4\,g} + 2\ SF_{6\,g} + 2\ H_{2\,g} + 3\ O_{2\,g}$ $\quad \Delta H_{rxn}$ = -2485 kJ
Energy is also released when oxygen reacts with calcium metal:
$2\ Ca_s + O_{2\,g} \rightarrow 2\ CaO_s$ $\quad \Delta H_{rxn}$ = -1270 kJ
Write the overall, balanced reaction so that the only products made are desired greenhouse gases and CaO and determine the enthalpy change.
($CO_{2\,g} + 8\ CaF_{2\,s} + 2\ SO_{3\,g} \rightarrow CF_{4\,g} + 2\ SF_{6\,g} + 8\ CaO_s$ $\quad \Delta H_{rxn}$ = 2577.5 kJ)

Use heat of formation data to verify the results of the Hess' Law problem.
ΔH_f ($CO_{2\,g}$) = -393.5 kJ/mol $\quad$ ΔH_f ($CF_{4\,g}$) = -933.6 kJ/mol
ΔH_f ($SO_{3\,g}$) = -396 kJ/mol $\quad$ ΔH_f (SF_6 g) = -1209 kJ/mol
ΔH_f (CaF_2) = -1228 kJ/mol $\quad$ ΔH_f (CaO_s) = - 635 kJ/mol

Another process can be added that converts CaO to $CaCO_3$. Write the reaction that could occur.
($CaO_s + CO_{2\,g} \rightarrow CaCO_{3\,s}$)
If ΔH_f ($CaCO_{3\,s}$) is -1207 kJ/mol, does converting CaO to $CaCO_3$ help reduce the energy requirements of this reaction?
(Yes, the production of 8 moles $CaCO_{3\,s}$ releases 1428 kJ, lowering the total reaction enthalpy to 1149.5 kJ.)