

1. The Stirling engine is a heat engine that absorbs heat from an external source. The working substance can be any gas. The engine consists of two cylinders with pistons, one in thermal contact with each reservoir (see Figure 1 below). Between the two cylinders is a passageway where gas flows past a regenerator whose temperature varies gradually from the hot side to the cold side. The heat capacity of the regenerator is very large, so its temperature is affected very little by the gas flowing past. The four steps of the engine's cycle are as follows:

- i. Power stroke. While in the hot cylinder at temperature  $T_h$ , the gas absorbs heat and expands isothermally, pushing the hot piston outward. The piston in the cold cylinder remains at rest, all the way inward as shown in the figure.
  - ii. Transfer to the cold cylinder. The hot piston moves in while the cold piston moves out, transferring the gas to the cold cylinder at constant volume. While on its way, the gas flows past the regenerator, giving up heat and cooling to  $T_c$ .
  - iii. Compression stroke. The cold piston moves in, isothermally compressing the gas back to its original volume as the gas gives up heat to the cold reservoir. The hot piston remains at rest, all the way in.
  - iv. Transfer to hot cylinder. The cold piston moves the rest of the way in while the hot piston moves out, transferring the gas back to the hot cylinder at constant volume. While on its way, the gas flows past the regenerator, absorbing heat until it is again at  $T_h$ .
- (a) Draw a  $PV$  diagram for this idealized Stirling cycle. (8%)
  - (b) Forget about the regenerator for the moment. Then, during step ii, the gas will give up heat to the cold reservoir instead of to the regenerator; during step iv, the gas will absorb heat from the hot reservoir. Calculate the efficiency of the engine in this case, assuming that the gas is ideal. Express your answer in terms of the temperature ratio  $T_c/T_h$  and the compression ratio (the ratio of the maximum and minimum volumes). Show that the efficiency is less than that of a Carnot engine operating between the same temperatures. (8%)
  - (c) Now put the regenerator back. Argue that, if it works perfectly, the efficiency of a Stirling engine is the same as that of a Carnot engine. (8%)
  - (d) Discuss, in some detail, the various advantages and disadvantages of a Stirling engine, compared to other engines. (6%)

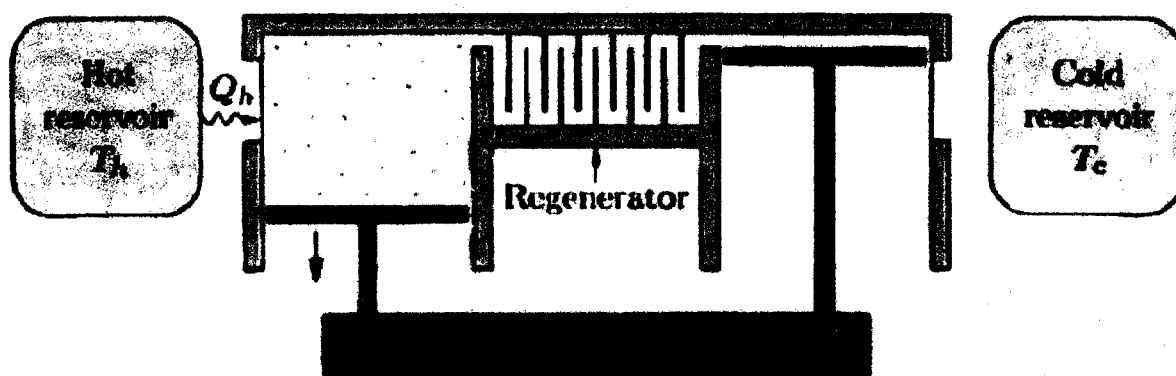
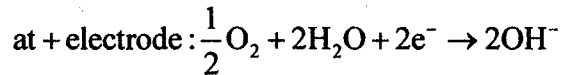
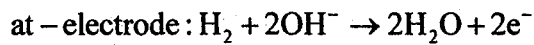


Figure 1. A Stirling engine, shown during the power stroke when the hot piston is moving outward and the cold piston is at rest.

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2. In a hydrogen fuel cell, the steps of the chemical reaction are

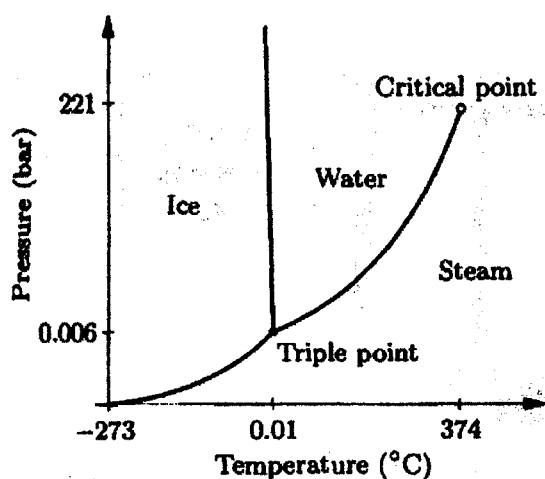


Suppose that the fuel cell is to be operated at 75°C and atmospheric pressure. We wish to estimate the maximum electrical work done by the cell, using only the room-temperature data in Table 1 (at the very end of exam sheet). Let us assume  $G$  for both  $\text{H}_2$  and  $\text{O}_2$  to be zero at 25°C.

- (a) Estimate the Gibbs free energy of a mole of  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  at 75°C. (8%)
- (b) Calculate the maximum electrical work done by the fuel cell at 75°C, for one mole of hydrogen fuel. Compare to the ideal performance of the cell at 25°C. (8%)
- (c) Calculate the voltage of the cell. (7%)
- (d) Assuming the atmospheric temperature is 25°C. Compare and comment on the efficiency of a Carnot engine, operating at the same temperature of the fuel cell, and the fuel cell. (7%)

3. A power plant produces 1 GW of electricity, at an efficiency of 40% (typical of today's coal-fired plants). Assuming the heat capacity of water at room temperature is 4.2 kJ/mol, and other phase transformation properties are shown in Figure 2.

- (a) At what rate does this plant expel waste heat into its environment? (8%)
- (b) Assume first that the cold reservoir for this plant is a river whose flow rate is  $100 \text{ m}^3/\text{s}$ . By how much will the temperature of the river increase? (8%)
- (c) To avoid this "thermal pollution" of the river, the plant could instead be cooled by evaporation of river water. At what rate must the water evaporate? What fraction of the river must be evaporated? (8%)



$T$ (°C)	$P_v$ (bar)	$L$ (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

**Figure 2.**  
Phase diagram for  $\text{H}_2\text{O}$  (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries).

4. The density of ice is  $917 \frac{\text{kg}}{\text{m}^3}$  and a phase diagram of water is shown in Figure 2.

- (a) Use the Clausius-Clapeyron relation to explain why the slope of the phase boundary between water and ice is negative. (8%)
- (b) How much pressure would you have to put on an ice cube to make it melt at  $-1^\circ\text{C}$ ? (8%)

**Table 1. Thermodynamics Properties of Selected Substances**

All of the values in this table are for one mole of material at 298 K and 1 bar. Following the chemical formula is the form of the substance, either solid (s), liquid (l), gas (g) or aqueous solution (aq). When there is more than one common solid form, the mineral name or crystal structure is indicated. Data for aqueous solutions are at a standard concentration of 1 mole per kilogram water. The enthalpy and Gibbs free energy of formation,  $\Delta_f H$  and  $\Delta_f G$ , represent the changes in  $H$  and  $G$  upon forming one mole of the material starting with elements in their most stable pure states (e.g., C (graphite),  $\text{O}_2$  (g), etc.). To obtain the value of  $\Delta H$  and  $\Delta G$  for another reaction, subtract  $\Delta_f$  of the reactants from  $\Delta_f$  of the products.

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	$S$ (J/K)	$C_P$ (J/K)	$V$ ( $\text{cm}^3$ )
$\text{H}_2$ (g)	0	0	130.68	28.82	
H (g)	217.97	203.25	114.71	20.78	
$\text{H}^+$ (aq)	0	0	0	0	
$\text{H}_2\text{O}$ (l)	-285.83	-237.13	69.91	75.29	18.068
$\text{H}_2\text{O}$ (g)	-241.82	-228.57	188.83	33.58	
He (g)	0	0	126.15	20.79	
Hg (l)	0	0	76.02	27.98	14.81
$\text{N}_2$ (g)	0	0	191.61	29.12	
$\text{NH}_3$ (g)	-46.11	-16.45	192.45	35.06	
$\text{Na}^+$ (aq)	-240.12	-261.91	59.0	46.4	-1.2
NaCl (s)	-411.15	-384.14	72.13	50.50	27.01
$\text{NaAlSi}_3\text{O}_8$ (albite)	-3935.1	-3711.5	207.40	205.10	100.07
$\text{NaAlSi}_2\text{O}_6$ (jadeite)	-3030.9	-2852.1	133.5	160.0	60.40
Ne (g)	0	0	146.33	20.79	
$\text{O}_2$ (g)	0	0	205.14	29.38	
$\text{O}_2$ (aq)	-11.7	16.4	110.9		
$\text{OH}^-$ (aq)	-229.99	-157.24	-10.75	-148.5	
Pb (s)	0	0	64.81	26.44	18.3
$\text{PbO}_2$ (s)	-277.4	-217.33	68.6	64.64	
$\text{PbSO}_4$ (s)	-920.0	-813.0	148.5	103.2	
$\text{SO}_4^{2-}$ (aq)	-909.27	-744.53	20.1	-293	
$\text{HSO}_4^-$ (aq)	-887.34	-755.91	131.8	-84	
$\text{SiO}_2$ ( $\alpha$ quartz)	-910.94	-856.64	41.84	44.43	22.69
$\text{H}_4\text{SiO}_4$ (aq)	-1449.36	-1307.67	215.13	468.98	

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