

"Thermodynamic Analysis of Processes for Hydrogen Generation by Decomposition of Water"

by

John P. O'Connell

Department of Chemical Engineering

University of Virginia

Charlottesville, VA 22904-4741

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Module 5: The Sulfur-Iodine Process for Thermochemical Hydrogen

Introduction

Module 1 of this series provides the foundation for thermodynamic analysis of processes for energy effects and process constraints. Module 2 provides experience with single-unit processes. Module 3 treats processes for thermochemical decomposition of water for hydrogen manufacture from an overall point of view. Module 4 gave experience in treating recycles and multiple sections involving reactions. The present module builds on the others to do a thermodynamic analysis of the Sulfur-Iodine process.

We first repeat essential elements of Module 1. Figure 5.1 illustrates the concept for a steady-flow system, with inlet and outlet streams at specified absolute temperatures, T , pressures, P , and sets of molar or mass amounts for the components, $\{N\}$, along with energy that crosses the boundaries as "shaft work", W_s , and heat, Q . Note that if a stream has both vapor and liquid, its specification must include the amounts of components in the phases. For pure components, this means specifying either T or P , the total flow, N , and the quality or fraction of the system that is vapor, x . For mixtures, defining the state is more elaborate. The balance equations for steady flow processes are:

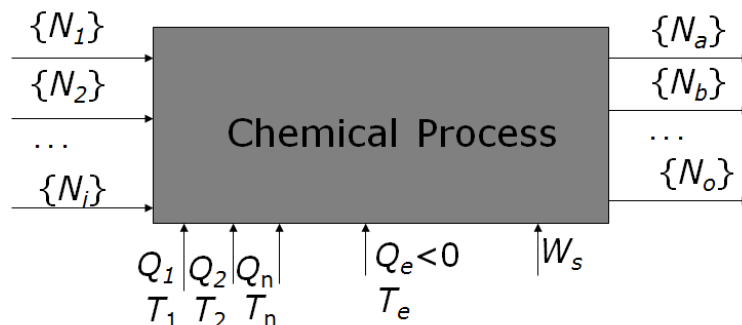


Figure 5.1. Steady Flow System for Applying Material, Energy, and Entropy Relations, Eqs. (5.1) and (5.2).

$$\sum_i N_i h_i(T_i, P_i, \{x\}_i) - \sum_o N_o h_o(T_o, P_o, \{x\}_o) + \sum_s W_s + \sum_b Q_b + Q_e = 0 \quad (5.1)$$

$$\sum_i N_i s_i(T_i, P_i, \{x\}_i) - \sum_o N_o s_o(T_o, P_o, \{x\}_o) + \sum_b \frac{Q_b}{T_b} + \frac{Q_e}{T_e} + S_{gen} = 0 \quad (5.2)$$

Here h is the molar enthalpy, s is the molar entropy, and $\{x\}$ is the set of component mole fractions found from the set of numbers of moles of components, $\{N\}$, in a stream. Kinetic and potential energy differences in the flowing streams have been ignored in Eq. (5.1). The summation \sum_i is over all input streams, i , and the summation \sum_o is over all output streams, o . Consequently, all molar flow numbers, $\{N\}_i$ and $\{N\}_o$, are positive. The summations \sum_s and \sum_b are for the work and heat effects, respectively, associated with external utilities. The species amounts, $\{N\}_i$ and $\{N\}_o$ are related by mass conservation; moles are conserved only in nonreacting systems.

These two relations express the conservation of energy among the forms generally treated in chemical processes, Eq. (5.1), and the balance of entropy, Eq. (5.2), which has entropy conservation for reversible cases ($s_{gen\ rev} = 0$) and positive entropy generation ($s_{gen} > 0$) in real systems. The heat effects, $\{Q_b\}$ and Q_e , are defined to be positive when heat is put in; they cross the outside of the system boundary (surroundings) at temperatures T_b and T_e . A reversible process gives the absolute upper limit, the best case, of the efficiency of energy usage. That is, when $s_{gen} = 0$, the solution to Eqs. (5.1) and (5.2) will give the minimum input shaft work, high-temperature heat, or energy-carrying material, to accomplish a process that does not occur spontaneously.

As shown in Module 4, when there are multiple sections, the fundamental equations are used for each section, with the streams and heat exchanges matched between connected sections. Care must be exercised to insure that the signs on the flows in the equations are appropriate; when they are positive in the relations for one section, they are negative in the relations for the connected section.

The two energy/entropy relations force two unknown quantities to be found from the known variable values, while giving consistency among molar flows for all chemical reactions occurring. Thus, as shown in Module 1, many different cases can be set up. However, for processes such as Sulfur-Iodine (S-I), only the three cases of Table 5.1 are implemented.

Table 5.1 Options for Specifications and Solution Variables for Eqs. (5.1) and (5.2) of Module 5.

Case	Specifications	Solution Variables
A	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}, \{Q_b\}^*, \{T_b\}, T_e, S_{gen}$	Q_e, Q_{bn}
D	$T_i, P_i, \{N\}_i, T_o, P_o, \{N\}_o, \{W_s\}, \{Q_b\}, \{T_b\}, T_e$	Q_e, S_{gen}
J	$\{T_i\}, \{P_i\}, \{N\}_i^*, \{T_o\}, \{P_o\}, \{N\}_o, \{W_s\}^*, \{Q_b\}, \{T_b\}, T_e, S_{gen}$	Q_e, N_{in}
* Includes all elements of set except n which is solved for		

Case V Example.

The S-I Process was conceived of in the 1970s, during the "first energy crisis", to provide massive amounts of Hydrogen as an alternative energy source for electricity through the use of fuel cells [2, 12]. Many papers on the process, including some with different thermodynamic approaches, have been published in the International Journal of Hydrogen Energy [13].

Figure 5.1 shows a flow diagram for the 3 sections, each of which involves one reaction. The H_2 and O_2 products leave Sections 3 and 2, respectively, while the other reaction species are

recycled, often with excesses of other substances (in parentheses). Unlike Module 4 where the streams exchanged between the sections are pure, mixtures are passed here, requiring complex thermodynamic property modeling [14].

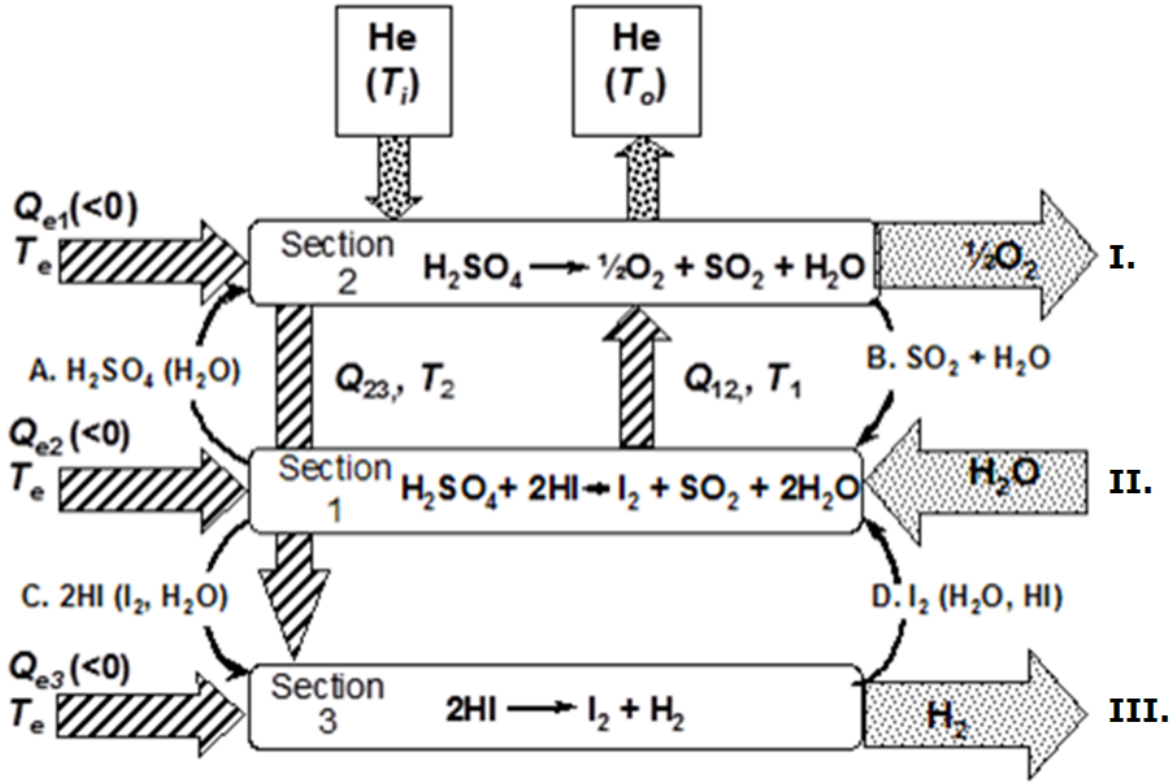


Figure 5.1 Sections of an idealized S-I Process showing inlet, outlet, and intersection streams and intersection and environmental heat flows [5].

The process has Section 2 which receives high temperature energy, from a Helium stream being cooled, to decompose the sulfuric acid (H_2SO_4) of input Stream A (perhaps along with excess H_2O), into the O_2 product of Stream I, as well as SO_2 and additional H_2O . Section 1 receives the latter as Stream B. There may be excess heat, which is transferred to Section 3 as Q_{23} .

In addition to stream B from Section 2, Section 1 also receives Stream D from Section 3 containing iodine, I_2 , (perhaps with excess H_2O and hydrogen iodide, HI) along with the process feed H_2O in Stream II. The reaction among these species, called the Bunsen Reaction, reforms the H_2SO_4 , as well as makes HI at a moderate temperature. With sufficient added H_2O , the Section 1 products break into two liquid streams, which are decanted to recycle the H_2SO_4 to Section 2 in Stream A, and put the HI into Section 3 (perhaps with excess H_2O and I_2) in Stream C. The reaction is exothermic, so some heat can be transferred to Section 2 as Q_{12} .

The HI decomposes in Section 3 to form the H_2 product in Stream III, as well as I_2 for recycle to Section 1 in Stream D. The decomposition requires energy at an elevated temperature; in this version it is Q_{23} .

All of the Sections are expected to reject heat to the environment, Q_{ei} where $i = 1, 2, \text{ or } 3$.

Completing an energy/entropy analysis of this process involves applying Eqs. (5.1) and (5.2) to all Sections, using the material and heat transfers connecting the Sections. Since stream properties will be computed using flowsheeting software, all that needs to be denoted are the total moles and molar properties of the streams, not those of individual species. Heat flows connecting Sections must have consistent signs.

The stream flows must be carefully treated. Helium is involved in only Section 2 and the basis is 1 kmol H₂ produced in Stream III of Figure 5.1. The reactions of Sections 1 and 2 are considered to completely convert the sulfur compounds. The atom balances from the reactions set some of the stream flows, but the amounts of H₂O in Streams A, N_{WA} , and C, N_{WC} , as well as the amounts of I₂ and HI in stream C, N_{IC} and N_{HIC} , can be arbitrarily set as shown in Eqs. (5.3).

$$\begin{aligned}
 N_A &= N_{WA} + 1 \\
 N_B &= N_A + 1 \\
 N_C &= N_{WC} + N_{IC} + N_{HIC} + 2 \\
 N_D &= N_C - 1
 \end{aligned}
 \tag{5.3}$$

Here the single subscripts refer to streams in Figure 5.1 and the double subscripts refer first to the species, H₂O (*w*), I₂ (*i*), and HI (*h*), and second to the stream.

Table 5.2 shows values of stream flows for various cases. Case 5 is like a proposed S-I design.

Table 5.2 Stream Flows, kmol, for S-I Process Cases for 1 kmol H₂O split into H₂ and O₂.

Case	N_{WA}	N_{WC}	N_{IC}	N_{HIC}	N_A	N_B	N_C	N_D
1	0	0	0	0	<i>1</i>	<i>2</i>	<i>2</i>	<i>1</i>
2	4	5	0	0	<i>5</i>	<i>6</i>	<i>7</i>	<i>6</i>
3	0	5	7	0				
4	4	5	7	4				
5	4	31	23	4				

Problem 5.1 Complete Table 5.2 for the molar flows of streams A - D when the moles of recycled species amounts N_{WA} , N_{WC} , N_{IC} , and N_{HIC} are specified.

The forms of Eqs. (5.1) and (5.2) for Section 2 are

$$(N_A h_A - N_B h_B) - N_O h_O + N(h_i - h_o) + Q_{12} - Q_{23} + Q_{e2} = 0 \tag{5.V1}$$

$$(N_{ASA} - N_{BSB}) - N_{OSO} + N(s_i - s_o) + \frac{Q_{12}}{T_1} - \frac{Q_{23}}{T_2} + \frac{Q_{e2}}{T_e} + N_{HS_{gen2}} = 0 \tag{5.V2}$$

Sections 1 and 3 do not have Helium flow. For Section 1, the relations become

$$(N_B h_B + N_D h_D - N_A h_A - N_C h_C) + N_W h_W - Q_{12} + Q_{e1} = 0 \tag{5.V3}$$

$$(N_{BSB} + N_{DSD} - N_{ASA} - N_{CSC}) + N_{WSW} - \frac{Q_{12}}{T_1} + \frac{Q_{e1}}{T_e} + N_{HS_{gen1}} = 0 \tag{5.V4}$$

while for Section 3 they are

$$(N_{ChC} - N_{DhD}) - N_{HhH} + Q_{23} + Q_{e3} = 0 \quad (5.V5)$$

$$(N_{CSc} - N_{DSD}) - N_{HSH} + \frac{Q_{23}}{T_2} + \frac{Q_{e3}}{T_e} + N_{HS_{gen3}} = 0 \quad (5.V6)$$

Helium can be considered an ideal gas under these conditions, so its enthalpy and entropy differences can be computed with Eqs. (5.4) and (5.5).

$$(h_o - h_i)^{ig} = \int_{T_i}^{T_o} c_p^{ig}(T) dT \quad (5.4)$$

$$(s_o - s_i)^{ig} = \int_{T_i}^{T_o} \frac{c_p^{ig}(T)}{T} dT - R \ln\left(\frac{P_o}{P_i}\right) \quad (5.5)$$

where $c_p^{ig}(T)$ is a constant, polynomial, or other integrable function of T .

Table 5.3 lists many of the variables of the Case V examples.

Table 5.3 Variables of Case V Examples.

Process Stream Variables	$T_A, P_A, N_{WA}, T_B, P_B, T_C, P_C,$
Helium Stream Variables	$N, T_i, P_i,$
Heat and Entropy Variables	$Q_{23}, T_2, Q_{e1}, Q_{e2}, S_{gen1},$

Number of independent variables = ____; number of solved variables = ____

Typical analysis variables to be found: _____

Typical design variables to be found: _____

Problem 5.2 Complete Table 5.3 to list all of variables to be specified and solved for in Case V examples. How many are independent and how many are solved for? Give typical solution variables for analysis and for design problems.

There is a sequential strategy for solving the relations, Eqs. (5.V1) - (5.V6), for a typical design problem. Case A is solved for Section 3 and for Section 1, and then Case J is solved for Section 2. For a typical analysis problem, Case D is solved for each Section independently.

Problems 5.3 Write relations to find the unknown variables for the typical design problem above.

$$Q_{e3} = \quad (5.VJ1)$$

$$Q_{23} = \quad (5.VJ2)$$

$$Q_{e1} = \quad (5.VJ3)$$

$$Q_{12} = \quad (5.VJ4)$$

$$N = \quad (5.VJ5)$$

$$Q_{e2} = \quad (5.VJ6)$$

Problems 5.4 Write relations to find the unknown variables for the typical analysis problem above.

$$Q_{e1} = \quad (5.VD1)$$

$$S_{gen1} = \quad (5.VD2)$$

$$Q_{e2} = \quad (5.VD3)$$

$$S_{gen2} = \quad (5.VD4)$$

$$Q_{e3} = \quad (5.VD5)$$

$$S_{gen3} = \quad (5.VD6)$$

Numerical Problems for Case V.

The problems below involve both design and analysis situations. Since stream compositions will vary, their properties will be required for each problem. Similar cases were described in [5], where multiple streams entered and left each section. Here a revised properties model [14] has been used and the streams are lumped as in Figure 5.1. The properties for the cases of Table 5.2 are given in Tables 5.4 and 5.5.

Table 5.4 Properties of Feed and Product Streams for an S-I Process as in Tables 3.2 and 4.2.

Stream	Component	T , K	P , MPa	h , MJ kmol ⁻¹	s , MJ kmol ⁻¹ K ⁻¹
I	H ₂ O	275.00 (l)	0.4	-287.20	-0.169
II	O ₂	346.57 (g)	0.4	-25.99	-0.007
III	H ₂	386.15 (g)	4	-7.32	-0.0230

Table 5.5 Properties of Streams for Problems about S-I Processes.

Stream	Variable\Problem #	1	2	3	4	5
A	T , K	393	393	393	393	393
	P , MPa	1.2	1.2	1.2	1.2	1.2
	h , MJ kmol ⁻¹	-806.4	-384.3	-806.4	-384.3	-384.3
	s , MJ kmol ⁻¹ K ⁻¹	-0.3765	-0.1850	-0.3765	-0.1850	-0.1850
B	T , K	393	393	393	393	393
	P , MPa	1.2	1.2	1.2	1.2	1.2
	h , MJ kmol ⁻¹	-293.5	-283.7	-293.5	-283.7	-283.7
	s , MJ kmol ⁻¹ K ⁻¹	-0.0887	-0.1226	-0.0887	-0.1226	-0.1226
C	T , K	373	373	373	373	373
	P , MPa	4	4	4	4	4
	h , MJ kmol ⁻¹	15.16	15.16	-90.9	-67.5	-138.8
	s , MJ kmol ⁻¹ K ⁻¹	0.0238	0.0238	-0.0212	-0.0106	-0.0512
D	T , K	425	425	425	425	425
	P , MPa	4	4	4	4	4
	h , MJ kmol ⁻¹	24.23	24.23	-89.8	-66.87	-137.0
	s , MJ kmol ⁻¹ K ⁻¹	0.0637	0.0637	-0.0105	0.0017	-0.0426

For all problems, $T_e = 313\text{K}$, $T_i = 1100\text{ K}$, $P_i = 4\text{ MPa}$, $T_o = 800\text{ K}$, $P_o = 4\text{ MPa}$, $T_1 = 393\text{ K}$, $T_2 = 550\text{ K}$, and $c_p^{ig}(T) = \frac{5}{2}R = 0.0208\text{ MJ kmol}^{-1}\text{ K}^{-1}$. For the design problems, set $s_{gen1} = 0.2\text{ MJ kmol}^{-1}\text{ K}^{-1}$, $s_{gen2} = 0.1\text{ MJ kmol}^{-1}\text{ K}^{-1}$, and $s_{gen3} = 0.2\text{ MJ kmol}^{-1}\text{ K}^{-1}$. For the analysis problems, set $N = 100\text{ kmol}$, $Q_{12} = -150\text{ MJ}$, and $Q_{23} = 200\text{ MJ}$. These generally lead to appropriate heat rejections, heat transfers, molar flows, and entropy generations.

Table 5.6 shows design problems for stream of Table 5.2 and properties of Tables 5.4 and 5.5.

Table 5.6 Solutions to Problems for Case VJ of Table 5.5.

Problem #	Q_{e1} , MJ	Q_{e2} , MJ	Q_{e3} , MJ	N , kmol	Q_{12} , MJ	Q_{23} , MJ
VJ.1	-668.0	500.2	-132.6	90.9	-742	119.1
VJ.2						
VJ.3						
VJ.4						
VJ.5						

For Problem VJ.1, Eqs. (5.VJ1) - (5.VJ6) become:

$$Q_{e3} = \frac{1[24.23-550(0.06373)]-2[15.16-550(0.0238)]+1[-7.32-550(-0.023)]+550(1)(0.2)}{(1-550/313)} = -132.6 \quad (5.VJ1.1)$$

$$Q_{23} = 1(24.23) - 2(15.16) + 1(-7.32) - (-132.6) = 119.1 \quad (5.VJ2.1)$$

$$Q_{e1} = \frac{1[-806.4-393(-0.3765)]+2[15.16-393(0.0238)]-2[-293.5-393(-0.0887)]-1[24.23-393(0.0637)]-1[-287.2-393(-0.169)]+393(1)(0.2)}{(1-393/313)} = -668 \quad (5.VJ3.1)$$

$$Q_{12} = 1(24.23) + 2(-293.5) - 1(-806.4) - 2(15.16) + 1(-287.2) + (-668) = -741.9 \quad (5.VJ4.1)$$

$$N = \frac{1[-806.4-313(-0.3765)]-2[-293.5-313(-0.0887)]-0.5[-25.99-313(-0.007)]-741.9(1-\frac{313}{393})-119.1(1-\frac{313}{550})-313(1)(0.1)}{[0.0208(800-1100)-313(0.0208)\ln(800/1200)]} = 90.9 \quad (5.VJ5.1)$$

$$Q_{e2} = 2(-293.5) + 0.5(-25.99) - 1(-806.4) + 119 - (-741.9) - 90.9(0.0208)(1100 - 800) = 500.2 \quad (5.VJ6.1)$$

Note that Q_{e2} is positive for Problem #V.1, indicating a heat addition from the surroundings, which is inappropriate. However, the total heat rejected is negative. This occurs because the entropy generated is small, leading to limited energy coming in with the Helium and inappropriate distribution of energy needs.

Problems 5.5 Complete Table 5.6 for the cases of Table 5.2 and the properties of Tables 5.4 and 5.5.

Problem 5.6 Verify that the Helium flow and total heat rejected in Problems #VD.1 - #VD.5 are the same as the overall analyses of Problem #IIIJ.3 of Module 3, as they must be.

Table 5.7 shows analysis problems with the stream flows of Table 5.2 and the properties of Tables 5.4 and 5.5.

Table 5.7 Specific Problems for Case VD.

Problem #	s_{gen1} , MJ kmol ⁻¹ K ⁻¹	s_{gen2} , MJ kmol ⁻¹ K ⁻¹	s_{gen3} , MJ kmol ⁻¹ K ⁻¹	Q_{e1} , MJ	Q_{e2} , MJ	Q_{e3} , MJ
VD.1	-0.185	0.495	0.311	-76.1	-67.6	-213.4
VD.2						
VD.3						
VD.4						
VD.5						

For Problem VD.1, Eqs. (5.VD1) - (5.VD6) become:

$$Q_{e1} = 1(-806.4) + 2(15.16) - 2(-293.5) - 1(24.23) - 1(-287.2) + (-150) = -76.1 \quad (5.VD1.1)$$

$$s_{gen1} = \{ [1(-0.3765) + 2(0.0238) - 2(-0.0887) - 1(0.06373) - 1(-0.169)] + \frac{-150}{393} - \frac{-76.1}{313} \} / 1 = -0.185 \quad (5.VD2.1)$$

$$Q_{e2} = 2(-293.5) - 1(-806.4) + 0.5(-25.99) - (-150) + (200) + 100(0.0208)(800 - 1100) = -67.6 \quad (5.VD3.1)$$

$$s_{gen2} = [2(-0.0887) - 1(-0.3765) + 0.5(-0.007) - \frac{-150}{393} + \frac{200}{550} - \frac{-67.8}{313} + 100(0.0208 \ln\{\frac{800}{1100}\})] / 1 = 0.495 \quad (5.VD4.1)$$

$$Q_{e3} = 1(24.23) - 2(15.16) + 1(-7.32) - 200 = -213.4 \quad (5.VD5.1)$$

$$s_{gen3} = [1(0.0637) - 2(0.0238) + 1(-0.023) - \frac{200}{550} - \frac{-213.4}{313}] / 1 = 0.311 \quad (5.VD6.1)$$

Note that Problem #VD.1 has negative entropy generated in Section 1, which is not possible. Increasing N would yield a feasible result, indicating that the energy input for Problem #VD.1 is not sufficient.

Problems 5.7 Complete Table 5.7 for the cases of Table 5.2 and the properties of Tables 5.4 and 5.5.

Problem 5.8 Verify that the total heat rejected and total entropy generated in Problems #VD.1 - #VD.5 are the same as the overall analyses of Problem #IIIA.3 of Module 3, as they must be.

Project 5.1 Obtain results for Problems 5.5 and 5.7 at other conditions. The following issues might be considered:

- Does increasing s_{gen} in one section affect the Helium flow more than in others?
- What happens to s_{gen} when the intersection heat transfers are changed?
- What happens to the efficiency and intersection heat transfers when the Helium temperatures are changed?
- What are the minimum conditions (N , Q_{12} , Q_{23}) to obtain appropriate heat rejection (negative Q_e) a