



# Chemical process systems analysis using thermodynamic balance equations with entropy generation. Revaluation and extension

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## ABSTRACT

Modeling inconsistencies exhibited in previous work (O'Connell, 2017) associated with post-combustion methanolamine (MEA) and ammonia (NH<sub>3</sub>) absorption processes have been revealed. The origin of the problem was that entropies for ionic reactions were not evaluated from input model equilibrium constants regressed from data. Revised calculations have been made using only properties of formation. Positive and consistent entropy generation rates ( $\dot{S}_{gen}$ ) are now found for all units and sections, and process convergence was achieved for multiple sections rather than for only single sections as before. Only minor changes in material, energy and overall  $\dot{S}_{gen}$  appeared in the new simulations. Results for  $\dot{S}_{gen}$  values show that the greatest irreversibilities for the MEA process are in the stripping section, though significant effects appear in the chiller, heat exchanger, and stripper flash. For the NH<sub>3</sub> process, roughly equal and large contributions to  $\dot{S}_{gen}$  are in the absorption, heat exchange, and stripping sections. Process improvements should focus on these sections. Applying the methodology to proposed changes would quantitatively reveal the amounts of increased efficiency.

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## 1. Introduction

An analysis of chemical processes using entropy generation was published previously (O'Connell, 2017). The fundamental relations for detailed thermodynamic analysis and their application were used for three processes of post-combustion carbon capture based on literature: membrane (Merkel et al., 2010), methanolamine (MEA) absorption (Ahn et al., 2013), and ammonia (NH<sub>3</sub>) absorption (Mathias et al., 2010). Each process was divided into sections connected by material streams giving energy and entropy flows, and the same material basis was used for all. While the overall analyzes for the latter two processes were consistent, the results for one section led to negative entropy generation ( $\dot{S}_{gen}$ ). For MEA absorption it was in the absorption section, while for NH<sub>3</sub> in the heat exchange section. At the time of publication, the source of these inconsistencies was unknown.

Investigation has been made into the calculations for thermodynamic properties of the complex ionic solution chemistry in these systems. Reaction-equilibrium constants can be put in as empirical temperature-dependent functions, or calculated from the thermodynamic quantities of reference state enthalpies and Gibbs energies of formation and heat capacities. For ions in solution, these are typically for infinite dilution in water. In early correlations, an em-

pirical temperature-dependent function was used, since it was assumed that this would be more accurate for fugacities and the enthalpies, which are of greatest interest to equilibrium process modeling. However, kinetic modeling is more challenging (Mathias and Gilmartin, 2014). The consequences were that entropies (*s*) became inconsistent because they were not rigorously evaluated from the equilibrium constants. Again, this was not an issue, because even though this thermodynamic property was tabulated, it was not used until the current approach was implemented. Recently, it was realized that calculating chemical equilibrium from the reference state thermodynamic properties did not cause the significant deterioration of model fitting, so they can now be used reliably (Mathias, 2017).

The present work describes recalculations of the two absorption processes with the previous procedures, with the software's embedded reference properties of formation and with the eNRTL activity coefficient model. These were applied to the streams for each unit in each process section to verify consistency and indicate sources of inefficiencies. Revised tables of results are given, typographical errors in the original work are noted, and more concrete discussion of process improvement options is presented.

It is now found that all absolute values of solution entropies are less negative, while  $\dot{S}_{gen}$  became positive for all process units and sections. Only small variations in overall results have been found for both processes, suggesting that calculational accuracy has not

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## Nomenclature

### Variables

$h$	molar enthalpy, MJ kmol <sup>-1</sup>
$\dot{H}$	enthalpy flow, MW
$\dot{n}$	molar flow rate, kmol s <sup>-1</sup>
$P$	Pressure, bar
$\dot{Q}$	heat flux, MW
$s$	molar entropy, kJ kmol <sup>-1</sup>
$\dot{S}_{gen}$	entropy generation rate, MW K <sup>-1</sup>
$T$	Temperature, K
$\dot{W}_S$	power, MW
$x$	mole fraction

### Subscripts

$B$	reboiler
$\text{CO}_2$	Carbon Dioxide
$e$	surroundings
$in$	into system
MEA	Methanolamine
$\text{N}_2$	Nitrogen
$\text{NH}_3$	Ammonia
$out$	out of system
$\text{H}_2\text{O}$	Water

been compromised. The consistency found allows examination of all process units, suggesting those which are most irreversible and appropriate for efficiency improvement.

## 2. Processes for post-combustion carbon capture

This section reanalyzes with entropy generation the two different absorption processes using essentially the same conditions to determine their relative  $\dot{S}_{gen}$  as well as to check the consistency of the properties models for cases where chemical solvents absorb  $\text{CO}_2$  and then are regenerated. The processes are 1) MEA absorption, based on the process of Ahn et al. (2013); and 2)  $\text{NH}_3$  absorption based on the process analyzed by Mathias et al. (2010). All cases used Aspen Version 9.0 for simulation of overall, section, and unit evaluations of stream compositions, as well as flow rates of materials, enthalpies and entropies. Here, instead of using temperature-dependent reaction constants, properties of formation for the various species in the reactions were used, along with the eNRTL parameters for activity coefficients.

Table 1 shows the principal external feeds and products, replacing Table 10 of the original paper. There is a slight difference in the amounts of  $\text{CO}_2$  product. The same calculational procedures have been followed. Typographical errors in the original paper tables have been corrected.

**Table 1**  
External steam conditions and properties for post-combustion carbon capture processes.

Stream name	Flue gas	Lean gas	$\text{CO}_2$ product (MEA)	$\text{CO}_2$ Product ( $\text{NH}_3$ )
$T$ , K	321.15	300	300	300
$P$ , bar	1	1	25	25
$\dot{n}$ , kmol s <sup>-1</sup>	20.04	16.13	2.19	2.10
$x_{\text{CO}_2}$	0.116	0.011	0.979	0.997
$x_{\text{H}_2\text{O}}$	0.110	0.028	0.019	0.003
$x_{\text{N}_2}$	0.774	0.961	0.002	0.000
$h$ , MJ kmol <sup>-1</sup>	-71.56	-10.96	-391.67	-393.95
$s$ , kJ kmol <sup>-1</sup> K <sup>-1</sup>	3.52	-1.45	-28.15	-25.61

### 2.1. Methanolamine absorption process

The most common post-combustion carbon capture processes absorb the  $\text{CO}_2$  via strong solvation with a chemical solvent such as an alkanolamine. A conventional methanolamine process evaluated by Ahn et al. (2013) is shown in Fig. 1, which has been slightly revised from the original (O'Connell, 2017) to correct a unit/stream omission and identify the units and streams more clearly. The properties model of Zhang et al. (2011) has been implemented.

As before, simulation of the whole plant together was not possible. However, convergence was obtained when the stream from the heat exchanger to the chiller was broken and other conditions were adjusted to make a very close match in properties and flows. While sensitivity from subtraction of large numbers caused up to 3% discrepancies in the properties and in the sums of the energy and entropy effects, this had no impact on conclusions about irreversibilities.

The conditions and properties at the internal section boundaries have some changes, so Table 2 lists the new values and those in Table 12 of the original paper. The recirculation rate has increased slightly but individual heat effects are a few percent lower. Table 3 lists new and previous (Table 13) energy and entropy results for the process sections. Supplementary Table S1 lists results for the 14 units. The overall process  $\dot{S}_{gen}$  became 0.29 MW K<sup>-1</sup>, compared to the previous 0.30 MW K<sup>-1</sup>. Since the section  $\dot{S}_{gen}$  all became positive, and their sum was consistent with the overall process result, evaluation of  $\dot{S}_{gen}$  could be done for each unit. Fig. 2(a) shows the relative contributions to the process  $\dot{S}_{gen}$  of the units and sections. It can be seen that the largest contributions are from the stripper and the flash to obtain the final  $\text{CO}_2$  product, suggesting where to focus process efficiency improvements.

As before, evaluation was done for the dependence on  $\dot{S}_{gen}$  of the overall process efficiency. The calculation sets  $\dot{S}_{gen}$  and then the stripping section heat requirement and the heat rejection rate are found. The calculated variations with  $\dot{S}_{gen}$  shown in Fig. 4 are similar to those found previously (Fig. 9). The short-dashed vertical line shows the revised  $\dot{S}_{gen}$  value as reported in Table 3. The value of  $\dot{S}_{gen}$  for the membrane process found previously was 0.467 MW K<sup>-1</sup>. Reducing  $\dot{S}_{gen}$  anywhere in the process by 10% reduces the stripping heat rate by 10% and the heat rejection rate by 7%. Preliminary studies show that reducing the stripper pressure and therefore the reboiler temperature, reduces entropy generation, improving efficiency.

### 2.2. Ammonia absorption process

Mathias et al. (2010) used thermodynamics and process simulations to evaluate the energy requirements for  $\text{NH}_3$  absorption to compare to those for amine absorption. There was no 2nd Law analysis in that work, but with small modifications of flow rates and other conditions, the previous work (O'Connell, 2017) allowed direct comparison of the  $\dot{S}_{gen}$  in that process to those of the membrane and methanolamine processes. Fig. 4 is a slight revision of Fig. 8 of the original paper to correct omissions and identify the units and streams more clearly. The properties model of Que and Chen (2011) has been implemented. The division into sections is generally similar to that for the amine absorption process of Fig. 1.

In the present case, the whole plant was able to be simulated together, so no mismatches of stream conditions arose. All of the section and unit  $\dot{S}_{gen}$  values were positive and consistent with the overall results. The conditions and properties at the section boundaries have significantly changed; Table 4 lists the new values and those in Table 15 of the original paper. Table 5 lists new and previous (Table 16) energy and entropy results for the process sections. Fig. 2(b) shows the relative contributions to the process  $\dot{S}_{gen}$  of the units and sections. In particular, the overall entropy generation has

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