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Heat of absorption of CO₂ with aqueous solutions of MEA: new experimental data

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Abstract

Heat of absorption of CO₂ and partial pressure of CO₂ with aqueous solutions of MEA has been measured in a reaction calorimeter CPA122 at 40, 80, and 120 °C for 30 wt% MEA solution and at 120 °C for 10 and 70 wt % MEA solutions. Heat of absorption measured in this work is also differential in loading, i.e. CO₂ has been added to the reactor in steps. An experimental set-up used by Kim and Svendsen (2007) has been used in this work after a small modification. Experiments show that heat of absorption depends both on loading and temperature, though the temperature dependency is not as high as was reported earlier. Application of the Gibbs –Helmholz correlation for the estimation of the heat of absorption based on experimental P_{CO₂} data is discussed.

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1. Introduction

CO₂ removal using solvent systems is the most widely used technology at present and 21 large-scale CCS projects reported to be under construction or in operation around the world can capture up to 40 million tons of CO₂ annually [1]. Lot of efforts are currently made to develop novel solvent systems in order to overcome the main drawback of this technology - high energy consumption for solvent regeneration. One of the important thermodynamic parameters necessary for the estimation of the energy consumption is a heat of absorption of CO₂, ΔH_{abs}. The exothermic reaction taking place when CO₂ is bound to the amine in the absorber generates a strong temperature bulge in the absorber. Basically, in flue gas treatment, all the reaction enthalpy leaves the plant with the

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treated flue gas, as solvent vapour, and is lost in the water wash knockout cooler. This implies that the reaction enthalpy must be supplied at stripper temperature in order to regenerate the solvent. In addition comes the need to generate stripping steam as sweep gas for the solvent, as given by the molar ratio between water and at the desorber top. This contribution to reboiler duty is given by the difference in between heat of absorption and heat of vaporization, where a high heat of absorption gives a stronger effect of temperature swing and may contribute in a reduced total reboiler duty. This always depends on the solvent properties and the chosen process configuration. Earlier work on measurement of the heat of absorption have shown that the values seen for amines considered in post combustion solvents have values within a relatively narrow range. However, recent work shows that there are still large differences arising through temperature effects. This was also discussed in early literature as e.g. in the paper by Crynes and Maddox, 1969 [2], where the heat of absorption for H₂S in MEA is shown to increase strongly with temperature.

Two types of calorimeters are used in literature for measuring the heats of absorption of CO₂ in different solvents. Experimental heats of absorption measured using *flow calorimeters* are normally differential in temperature, since experiments are performed at constant temperature. However, they are integral in loading, since the measurements are done by mixing fresh amine solution (zero loading) and CO₂ to a certain loading point. These data show little or no effect of loading on the heat of absorption [3]. *Reaction calorimeter* allows measurements of the heats of absorption differential both in temperature and loading by conducting experiments at constant temperature and adding CO₂ in several steps. Experimental heats of absorption of CO₂ with 30 wt% MEA solutions have been reported earlier by Kim and Svendsen, 2007 [4]. The same set-up has been used in this work after some modifications and new experimental data are presented in this work.

2. Experimental set-up and procedure

Ethanolamine (MEA, ≥99%, CAS 141-43-5) from Sigma Aldrich and CO₂ (5.0) from YARA were used as received. Aqueous solutions were prepared by gravity using distilled de-ionized water.

The experimental set-up (Fig. 1) and procedure have been described in detail by Kim and Svendsen, 2007 [4] and only briefly described here. The reaction calorimeter CPA 122 (Chemisens) is a mechanically agitated reactor of 2 L volume. The same set-up was used in this work after a small modification: the CO₂ in this work has been fed through the bottom of the reactor directly into the liquid phase instead of feeding through the reactor top into the vapour phase as has been done earlier. Also the CO₂ flow-meter was recalibrated and the amount of CO₂ fed to the reactor was calculated from the flow-meter data in addition to the estimation of the CO₂ amount based on the pressure drop in the CO₂ cylinders using Peng-Robinson EOS.

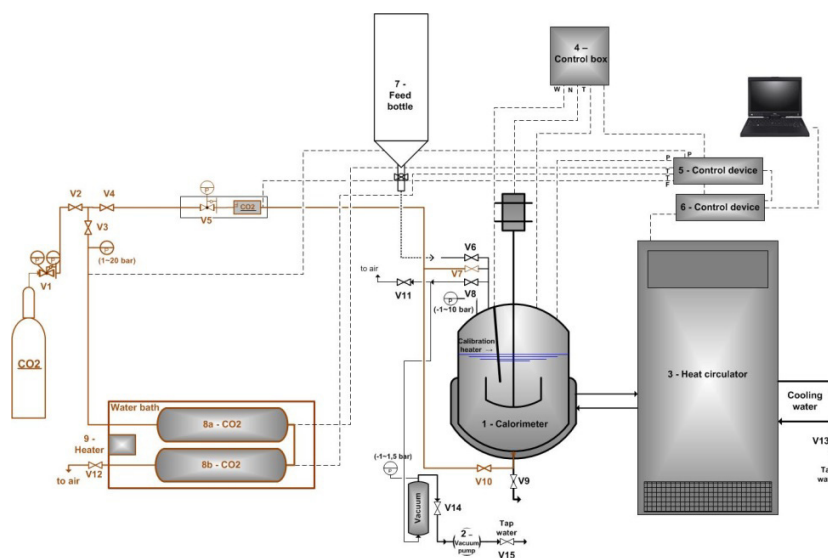


Figure 1. Experimental set-up for heat of absorption measurements

The temperature in the reactor is measured with a Pt100 temperature sensor (accuracy ± 0.1 K at 273 K, ± 0.027 K at 373 K); pressure transducer OMEGA (0-10 bara, 0.15% FS) is used for pressure measurements. Calorimetric sensitivity given by the producer is 0.1 W. Temperature, pressure, heat flow and other operation parameters are logged and recorded at 10 sec interval. The amount of heat released during the addition of CO_2 and the amount of CO_2 added were calculated by integrating the heat flow and CO_2 flow curves. Liquid sample was taken at the end of experiment and analysed for total alkalinity and CO_2 . Difference in CO_2 loading from the liquid analysis and flowmeter readings was within 5 %.

Equilibrium partial pressure of CO_2 was calculated from the total pressure data at each loading assuming that partial pressure of (amine + water) remains constant during the experiment and is equal to the total pressure in the reactor before the first addition of CO_2 .

3. Results and discussion

3.1. Heat of absorption of CO_2

To validate modifications to the set-up, the heat of absorption of CO_2 was measured with 30 wt% MEA solution at 40, 80, and 120 °C. The new experimental data are presented in Table A1-1 in the Appendix A1 and compared to the earlier data from ref. [4] in Fig. 2.

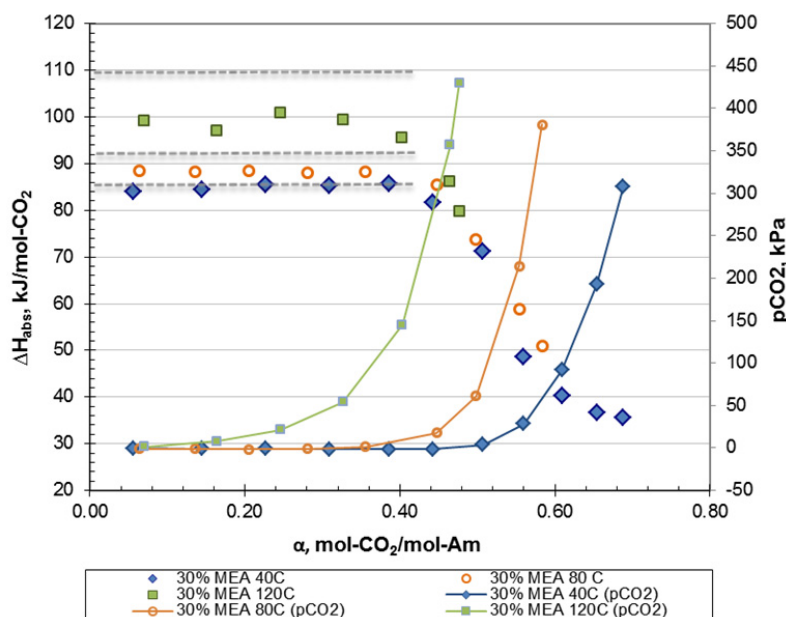


Figure 2. Heat of absorption of CO_2 and partial pressure CO_2 for 30 wt% MEA solution at 40, 80, and 120 °C measured in the reaction calorimeter. Dashed lines: average heats of absorption for loadings up to 0.4 mol- CO_2 /mol-Am reported in the ref. [4] for 40, 80, and 120 °C: 84.3, 92.4, 109.8 kJ/mol- CO_2 correspondingly.

For MEA it has been seen by several investigators that the heat of absorption shows an increase with temperature. This is due to the relatively strong temperature effect in the carbamate formation reaction [3]. It may be seen from the Fig. 2 that heat of absorption data measured in this work show weaker temperature dependence: data at 80 and 120 °C from this work are correspondingly 5 and 10% lower than reported earlier. No reasonable explanation was found for this behaviour and measurements with other solvent systems were done and compared to earlier data. No effect from the way of CO_2 feeding was observed when solutions with higher concentrations were used. As an example, heats of absorption for a solvent system with the total amine concentration of 50 wt% (Solvent A) are presented in Fig. 3. As may be seen, the temperature effect in the new experimental data is similar as the data

measured earlier, even if the new data give somewhat higher absolute value.

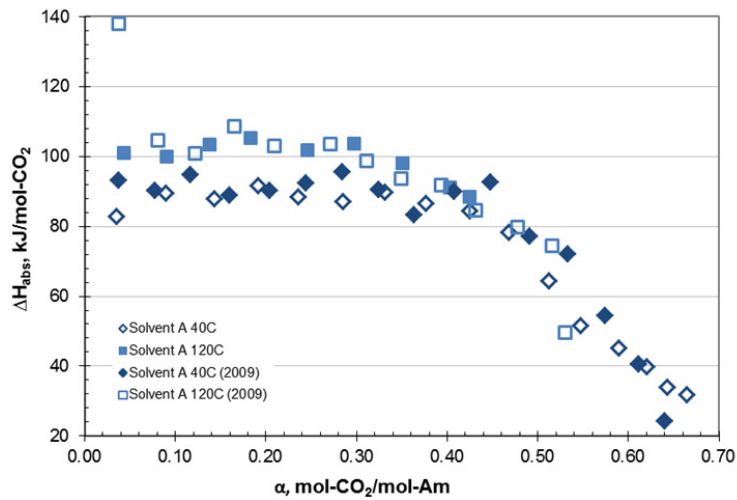


Figure 3. Heat of absorption of CO₂ with Solvent A at 40 and 120 °C compared to the earlier measurements (internal data).

It was assumed that solvent concentration may have an effect in case of MEA and experiments with 10 and 70 wt% MEA solutions have been performed at 120 °C. CO₂ in these experiments was fed through the bottom valve except for the loading points 3 when CO₂ was fed through the top valve (see Fig. 4 and Table A1-2).

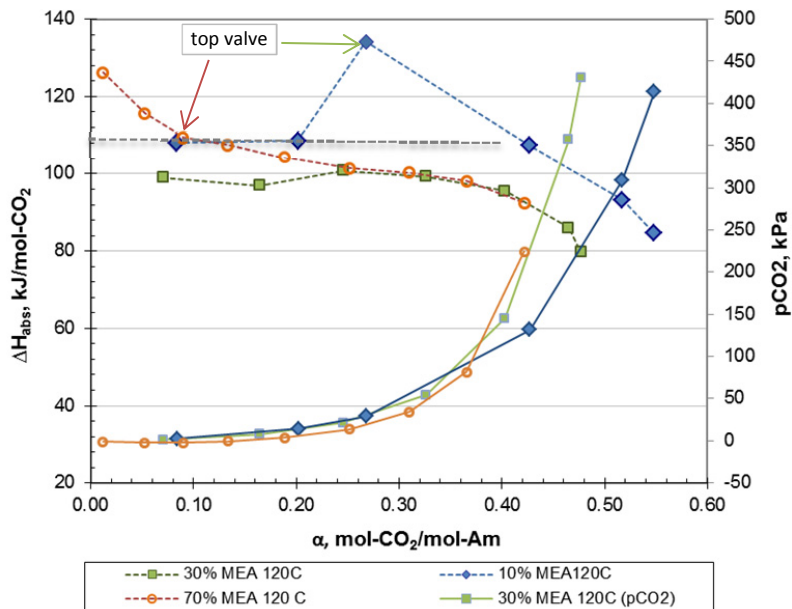


Figure 4. Heat of absorption of CO₂ and partial pressure of CO₂ for 10, 30, and 70 wt% MEA solution at 120 °C. For 10 and 70 wt% MEA loading point 3 (filled red) were obtained using the top valve for CO₂ feeding. For 30 wt% MEA: dashed line represents the data measured using the top valve, green data points measured using the bottom valve for CO₂ feeding.

As expected, at low concentration (10 wt %) of MEA much higher heat of absorption was measured when the CO₂ was fed from the top valve, although no effect was observed for 70 wt% MEA solution. It may be seen also

from the Fig. 4 that for the 70 wt% MEA solution, heat of absorption shows stronger dependence on loading below about 0.25 mol-CO₂/mol-MEA; after this loading, the heat of absorption is same as for the 30 wt% MEA.

3.2. Vapor-liquid equilibrium (VLE)

Partial pressure of CO₂ measured in the calorimeter for MEA solutions is presented in the Fig. 5a-b below. It may be also seen from the results presented in Tables A1-1 and A1-2 that in some cases the assumption of constant partial pressure of amine and water is not valid, resulting in negative values for p_{CO₂} at low loadings. In fact partial pressure of amine decreases with loading since concentration of the free amine in the solution decreases. However, when the partial pressure of CO₂ in the system is high enough compared to the solvent vapour pressure, the assumption may be used and a very good agreement with literature data may be seen from the Fig. 5a. Effect of amine concentration on the partial pressure of CO₂ at 120 °C may be seen in the Fig 5b. It may be seen from the figure that curves cross each other. This was also observed by Aronu et al. [6] at lower temperatures.

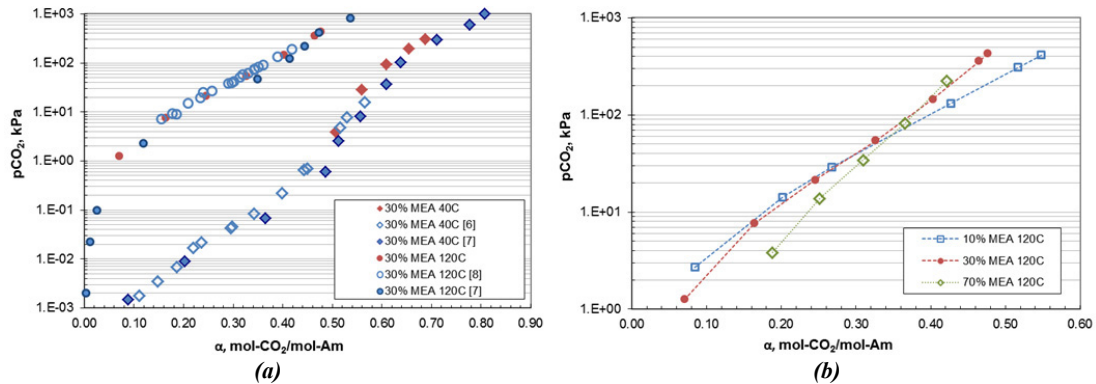


Figure 5. Partial pressure of CO₂ for 30 wt% MEA solution at 40, 80, and 120 °C compared to literature data (a) and for 10, 30, and 70 wt% MEA at 120 °C (b)

3.3. Consistency between VLE and calorimetric data

An expression derived from the Gibbs-Helmholtz (G-H) or the van't Hoff equation [9] is often used for the estimation of the heat of absorption based on experimental VLE data:

$$\left(\frac{\partial \ln p_{CO_2}}{\partial (1/T)} \right)_p = \frac{\Delta H}{R} \quad (1)$$

The derivation starts with the following relation for reactions in a closed system:

$$\left(\frac{\partial \Delta G}{\partial T} \right)_p = -\Delta S \quad (2)$$

By introducing the definition of Gibbs free energy:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (3)$$

and combination and differential calculus, the Gibbs Helmholtz equation results in [10]:

$$\left(\frac{\partial}{\partial T} \left(\frac{\Delta G}{T} \right) \right)_p = -\frac{\Delta H}{T^2} \quad (4)$$

Further, introduction of $\Delta G = -RT \ln K_{eq}$ gives:

$$\left(\frac{d \ln K_{eq}}{d(1/T)} \right)_p = \frac{\Delta H}{R} \quad (5)$$

When CO₂ is absorbed in MEA solution, carbamate is the dominating reaction:



Including the phase equilibrium ($\phi_{\text{CO}_2} p_{\text{CO}_2} = H \gamma_{\text{CO}_2} x_{\text{CO}_2}$), the thermodynamic equilibrium constant is given by:

$$K_{\text{MEA}} = \frac{x_{\text{MEAH}^+} x_{\text{MEACOO}^-}}{H x_{\text{CO}_2} x_{\text{MEA}}^2} \frac{\gamma_{\text{MEAH}^+} \gamma_{\text{MEACOO}^-}}{\phi_{\text{CO}_2} \gamma_{\text{MEA}}^2} \quad (7)$$

The equilibrium relation shows that $\ln K_{eq, \text{MEA}}$ will give a total reaction enthalpy a sum of the contribution from reaction under reference state conditions in the liquid phase, heat of dissolution (through the Henry's constant) and non-ideal mixing (through γ_i), gas phase non-ideality (through ϕ_i). It should also be noted that the derivation should be performed at constant pressure. Therefore, in order to get from the Gibbs-Helmholtz equation to the relation used in literature for estimation of delta H from p_{CO_2} vs. loading data, the following assumptions must be introduced:

1. Ideal gas phase ($\phi_i = 1$) implying low P
2. Liquid phase mole fraction relation independent of T/speciation independent of T.
3. No temperature effect on the non-ideal mixing effects/ratio of activity coefficients independent from T.

In addition, as pointed out by Sherwood and Prausnitz [12] in a derivation of the similar relation only for physical solubility of gases, the following is also assumed:

4. The solvent is essentially non-volatile at the temperature of derivation.

The validity of these assumptions is questionable. Assumption 2 is not too unreasonable when looking at typical speciation plot for e.g. MEA and MDEA, while assumption 3 is more uncertain. An earlier paper by Kim et al. [3] is based upon a consistent derivation of the equilibrium constants according to Eq. (5), with activity coefficients based upon Desmukh-Mather model. The same equilibrium model has been used in the current work. Reaction enthalpy for the individual reactions are given in Fig. 6 based only upon derivation of the equilibrium constants, thus neglecting the non-ideal mixing effects. The Heat of absorption (dH_{abs} in Fig. 6) according to Eq. (6) is calculated as the sum of $\Delta H_{\text{Dissolution}}$, $\Delta H_{\text{Protonation}}$ and $\Delta H_{\text{Carbamate formation}}$.

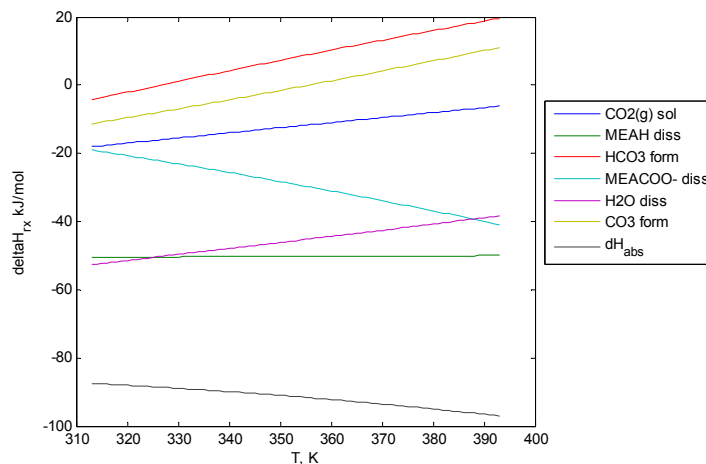


Figure 6. Heat of reaction for individual equilibrium reactions in the system CO₂/MEA/water as function of temperature

As can be seen from the figure the enthalpy of absorption calculated in this manner is very close to the results achieved in the calorimeter in this work, even with the assumption of negligible contribution from liquid phase non-idealities. It should also be noted that for MEA, the temperature effect is dominating by the enthalpy of carbamate formation. The equilibrium constant for carbamate formation is the most uncertain of all the reactions involved, and most commonly results from parameter adjustments in a thermodynamic model [3]. It may thus be claimed that an accurate model for temperature dependency of the heat of absorption is still not established.

To further test the values effect of deriving experimental p_{CO_2} data for MEA, the experimental data from Aronu et al. [6] was fitted to a correlation by Mejdell et al. [12]. Heat of absorption was estimated using Eq. (1). The result is shown in Fig. 7a. It is seen that the values are lower than in the calorimeter and also lower than the estimate from individual equilibrium constants. The effect of loading shows the strong sensitivity to the chosen model for the fit of p_{CO_2} vs. CO₂-loading.

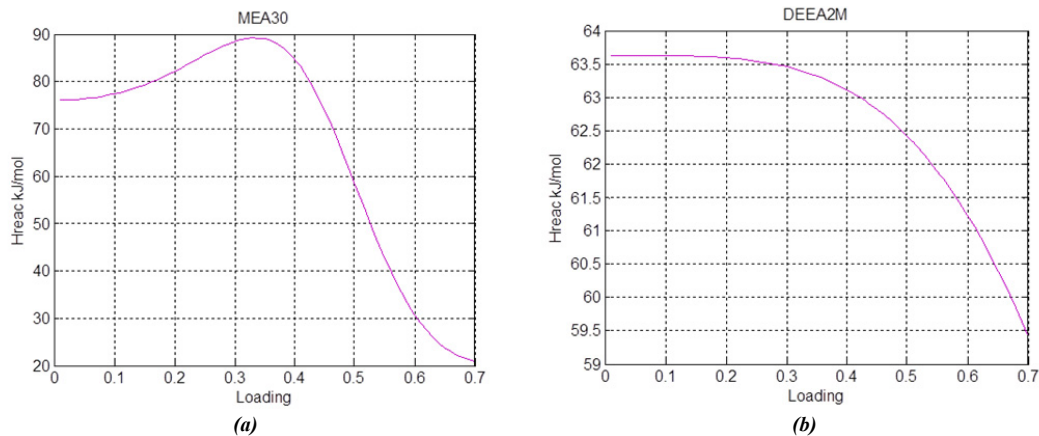


Figure 7. Heat of absorption of CO₂ based upon derivation of p_{CO_2} vs. temperature for 30 wt% MEA (a) and 2M (23 wt%) DEEA (b) solutions.

Finally, similar test is done with the tertiary amine DEEA. As given by Monteiro et al. [13], this amine is strongly hydrophobic and has strong activity effects with γ_{DEEA} (Raoult's law reference state) ranging from 10 to 25

depending on amine concentration and temperature. One should therefore think that derivation of the ΔH_{abs} from p_{CO_2} data for DEEA would fail according to the assumption 3 above. Calorimetric data for DEEA have been measured by Arshad et al. (2014). Experiments at 40 °C gave heat of absorption value close to -60 kJ/mol-CO₂, while a strong increase with temperature was found, with -100 kJ/mol-CO₂ at 80 °C. A derivation of p_{CO_2} data using a similar correlation as for MEA gives a value close to the result for 40 °C in the calorimeter. No temperature dependence can be obtained using this method as has been shown also earlier [4].

This shows that the derivation of p_{CO_2} gives a relatively robust estimate of the heat of absorption at low temperature, even for strongly non-ideal systems. However the strong increase with temperature cannot be validated and it should be concluded that significant uncertainty still remains w.r.t. temperature effects in heat of absorption.

Mathias and O'Connell [9] used a similar approach and analyzed a large number of experimental equilibrium and calorimetric data for CO₂ absorption in aqueous MEA. The authors concluded that there is an inconsistency between the VLE and calorimetric data for MEA in literature, that means that either one or both sets of data are incorrect or biased, but they could not identify which data set is inaccurate and suggested that new calorimetric data are necessary at temperatures of 373K and above and new VLE data at temperatures of 393K and above.

4. Conclusions

Heat of absorption of CO₂ and partial pressure of CO₂ with aqueous solutions of MEA has been measured in a reaction calorimeter CPA122 at 40, 80, and 120 °C for 30 wt% MEA solution and at 120 °C for 10 and 70 wt % MEA solutions. In this work CO₂ was fed into the liquid phase (reactor bottom) which resulted in lower heats of absorption for some solvents at high temperature compared to the heats of absorption measured for the same solvents with CO₂ fed into the vapour phase (reactor top). This difference was observed at high temperatures (80 and 120 °C) for low amine concentration. Application of the Gibbs –Helmholz correlation for the estimation of the heat of absorption based on experimental p_{CO_2} data is discussed. It is shown that the derivation of p_{CO_2} gives a relatively robust estimate of the heat of absorption at low temperature, even for strongly non-ideal systems. However the temperature dependence cannot be validated using this method and it should be concluded that significant uncertainty still remains with regard to temperature effects in the heat of absorption.

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Appendix A1.

Table A1- 1 Heat of absorption of CO₂ and partial pressure of CO₂ for 30 wt % MEA solution

Loading mol-CO ₂ /mol- Am	ΔH_{abs} kJ/mol-CO ₂	ΔH_{abs} kJ/mol-Am	pCO ₂ kPa	Loading mol-CO ₂ /mol- Am	ΔH_{abs} kJ/mol-CO ₂	ΔH_{abs} kJ/mol-Am	pCO ₂ kPa
40 °C				0.20	88.52	18.12	-1.62
0.06	84.03	4.69	-0.54	0.28	88.05	24.79	-0.76
0.15	84.36	12.23	-0.87	0.36	88.27	31.43	1.62
0.23	85.44	19.19	-0.98	0.45	85.55	39.28	18.14
0.31	85.36	26.20	-1.41	0.50	73.71	43.02	61.19
0.39	85.76	32.83	-1.41	0.55	58.94	46.30	214.20
0.44	81.55	37.44	-1.41	0.58	51.05	47.80	380.96
0.51	71.30	42.05	3.80	120 °C			
0.56	48.60	44.60	28.54	0.07	99.08	6.98	1.26
0.61	40.24	46.60	91.96	0.16	96.95	16.06	7.65
0.65	36.67	48.23	192.83	0.25	100.77	24.27	21.32
0.69	35.51	49.45	308.14	0.33	99.28	32.30	54.28
80 °C				0.40	95.55	39.60	145.30
0.06	88.55	5.67	-0.97	0.46	86.05	44.91	357.11
0.14	88.25	11.93	-1.19	0.48	79.74	45.88	430.36

Table A1- 2. Heat of absorption of CO₂ and partial pressure of CO₂ for 10 and 70 wt% MEA solutions measured at 120 °C

Loading mol-CO ₂ /mol- Am	ΔH_{abs} kJ/mol-CO ₂	ΔH_{abs} kJ/mol-Am	pCO ₂ kPa	Loading mol-CO ₂ /mol- Am	ΔH_{abs} kJ/mol-CO ₂	ΔH_{abs} kJ/mol-Am	pCO ₂ kPa
10 wt% MEA				70 wt% MEA			
0.08	108.17	9.10	2.70	0.01	126.25	1.50	-1.09
0.20	108.73	21.90	14.20	0.05	115.63	6.21	-2.30
0.27	<u>134.14*</u>	30.75	29.10	0.09	<u>109.47*</u>	10.33	-2.30
0.43	107.27	47.85	131.40	0.13	107.65	15.01	-0.55
0.52	93.29	56.20	309.50	0.19	104.41	20.71	3.82
0.55	84.60	58.86	413.90	0.25	101.49	27.09	13.84
				0.31	100.33	32.96	34.39
				0.37	98.07	38.43	81.46
				0.42	92.50	43.64	224.54

*data points measured using top valve for CO₂ feeding