

CAPE1330 MASS AND ENERGY BALANCES

Mixing and Solution

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General procedures

1. **Perform** all the required mass balance calculations

2. **Use** the appropriate form of the energy balances

$$\text{closed system: } Q + W = m\Delta\hat{U} + m\Delta\hat{E}_k + m\Delta\hat{E}_p$$

$$\text{open system: } \dot{Q} + \dot{W}_s = \dot{n}\Delta\hat{H} + \dot{n}\Delta\hat{E}_k + \dot{n}\Delta\hat{E}_p$$

3. **Choose** a reference state (phase, temperature and pressure) for each species involved in the process

4. **Calculate** all the required values of m , \dot{n} , \hat{U}_i or \hat{H}_i

5. **Solve** the mass and energy balances for unknown variables

Heat of solution

When two different liquids are mixed or when a gas or solid is dissolved in a liquid, bonds are broken between neighboring molecules and possibly between atoms of the feed materials, and new bonds are formed between neighboring molecules or ions in the product solution.

Suppose you mix 1 mole of **pure** liquid sulfuric acid with water at a specified temperature and pressure and then cool the mixture at constant pressure to bring it back to the initial temperature. The energy balance for this process is

$$Q = \Delta H = H_{H_2SO_4(aq)} - (H_{H_2SO_4(l)} + H_{H_2O(l)})$$

The difference between the enthalpy of the **aqueous solution** at the specified temperature and pressure and the total enthalpy of the **pure** solute and solvent at the same temperature and pressure is the **heat of solution** at that temperature and pressure.

Definitions

The **heat of solution** $\Delta\hat{H}_s(T, r)$ is defined as the change in enthalpy for a process in which 1 mole of a solute (gas or solid) is dissolved in r moles of a liquid solvent at a constant temperature T . As r becomes large, $\Delta\hat{H}_s$ approaches a limiting value known as the **heat of solution at infinite dilution**.

The **heat of mixing** has the same meaning as the heat of solution when the process involves mixing two fluids rather than dissolving a gas or solid in a liquid.

Perry's Chemical Engineers' Handbook gives heats of solution, **heat evolved** in kcal per mole, of various substances in water at either 18°C or "room temperature" which is roughly 25°C.

Table B.11 lists values of the heats of solution at 25°C of HCl(g) and NaOH(s) in water, and the heat of mixing at 25°C of H₂SO₄(l) and water.

Perry's handbook

TABLE 2-182 Heats of Solution of Inorganic Compounds in Water (Continued)

Substance	Dilution°	Formula	Heat, kcal/mol	Substance	Dilution°	Formula	Heat, kcal/mol
Lithium—(Cont.)				Phosphoric acid, ortho-	400	H ₃ PO ₄	+2.79
	∞	LiCl·H ₂ O	+4.45		400	H ₃ PO ₄ ·½H ₂ O	−0.1
	∞	LiCl·2H ₂ O	+1.07	pyro-	aq	H ₄ P ₂ O ₇	+25.9
fluoride	∞	LiCl·3H ₂ O	−1.98		aq	H ₄ P ₂ O ₇ ·1½H ₂ O	+4.65
hydroxide	∞	LiF	−0.74	Potassium acetate	∞	KC ₂ H ₃ O ₂	+3.55
	∞	LiOH	+4.74	aluminum sulfate	600	KAl(SO ₄) ₂	+48.5
	∞	LiOH·½H ₂ O	+4.39		600	KAl(SO ₄) ₂ ·3H ₂ O	+26.6
	∞	LiOH·H ₂ O	+9.6			KAl(SO ₄) ₂ ·12H ₂ O	−10.1
iodide	∞	LiI	+14.92	bicarbonate	2000	KHCO ₃	−5.1
	∞	LiI·½H ₂ O	+10.08	bromate	∞	KBrO ₃	−10.13
	∞	LiI·H ₂ O	+6.93	bromide	∞	KBr	−5.13
	∞	LiI·2H ₂ O	+3.43	carbonate	∞	K ₂ CO ₃	+6.58
	∞	LiI·3H ₂ O	−0.17			K ₂ CO ₃ ·½H ₂ O	+4.25
nitrate	∞	LiNO ₃	+0.466			K ₂ CO ₃ ·1½H ₂ O	−0.43
	∞	LiNO ₃ ·3H ₂ O	−7.87	chlorate	∞	KClO ₃	−10.31
sulfate	∞	Li ₂ SO ₄	+6.71	chloride	∞	KCl	−4.404
	∞	Li ₂ SO ₄ ·H ₂ O	+3.77	chromate	2185	K ₂ CrO ₄	−4.9
				chrome sulfate	600	KCr(SO ₄) ₂	+55
Magnesium bromide	∞	MgBr ₂	+43.7			KCr(SO ₄) ₂ ·H ₂ O	+42
	∞	MgBr ₂ ·H ₂ O	+35.9			KCr(SO ₄) ₂ ·2H ₂ O	+33
	∞	MgBr ₂ ·6H ₂ O	+19.8			KCr(SO ₄) ₂ ·6H ₂ O	+7
chloride	∞	MgCl ₂	+36.3			KCr(SO ₄) ₂ ·12H ₂ O	−9.5
	∞	MgCl ₂ ·2H ₂ O	+20.8	cyanide	200	KCN	−3.0
	∞	MgCl ₂ ·4H ₂ O	+10.5	dichromate	1600	K ₂ Cr ₂ O ₇	−17.8
	∞	MgCl ₂ ·6H ₂ O	+3.4	fluoride	∞	KF	+3.96
iodide	∞	MgI ₂	+50.2		∞	KF·2H ₂ O	−1.85
nitrate	∞	Mg(NO ₃) ₂ ·6H ₂ O	−3.7		∞	KF·4H ₂ O	−6.05
phosphate	aq	Mg ₃ (PO ₄) ₂	+10.2	hydrosulfide	∞	KHS	+0.86
sulfate	∞	MgSO ₄	+21.1		∞	KHS·½H ₂ O	+1.21
	∞	MgSO ₄ ·H ₂ O	+14.0	hydroxide	∞	KOH	+12.91
	∞	MgSO ₄ ·2H ₂ O	+11.7		∞	KOH·¾H ₂ O	+4.27
	∞	MgSO ₄ ·4H ₂ O	+4.9		∞	KOH·H ₂ O	+3.48
	∞	MgSO ₄ ·6H ₂ O	+0.55		∞	KOH·7H ₂ O	+0.86
	∞	MgSO ₄ ·7H ₂ O	−3.18	iodate	∞	KIO ₃	−6.93
sulfide	aq	MgS	+25.8	iodide	∞	KI	−5.23
Manganic nitrate	400	Mn(NO ₃) ₂	+12.9	nitrate	∞	KNO ₃	−8.633
	400	Mn(NO ₃) ₂ ·3H ₂ O	−3.9	oxalate	400	K ₂ C ₂ O ₄	−4.6
	400	Mn(NO ₃) ₂ ·6H ₂ O	−6.2			K ₂ C ₂ O ₄ ·H ₂ O	−7.5

Table B.11

$r(\text{mol H}_2\text{O/mol solute})$	$(\Delta\hat{H}_s)_{\text{HCl(g)}}$ kJ/mol HCl	$(\Delta\hat{H}_s)_{\text{NaOH(s)}}$ kJ/mol NaOH	$(\Delta\hat{H}_m)_{\text{H}_2\text{SO}_4}$ kJ/mol H_2SO_4
0.5	—	—	−15.73
1	−26.22	—	−28.07
1.5	—	—	−36.90
2	−48.82	—	−41.92
3	−56.85	−28.87	−48.99
4	−61.20	−34.43	−54.06
5	−64.05	−37.74	−58.03
10	−69.49	−42.51	−67.03
20	−71.78	−42.84	—
25	—	—	−72.30
30	−72.59	−42.72	—
40	−73.00	−42.59	—
50	−73.26	−42.51	−73.34
100	−73.85	−42.34	−73.97
200	−74.20	−42.26	—
500	−74.52	−42.38	−76.73
1 000	−74.68	−42.47	−78.57
2 000	−74.82	−42.55	—
5 000	−74.93	−42.68	−84.43
10 000	−74.99	−42.72	−87.07
50 000	−75.08	−42.80	—
100 000	−75.10	—	−93.64
500 000	—	—	−95.31
∞	−75.14	−42.89	−96.19

Hypothetical process

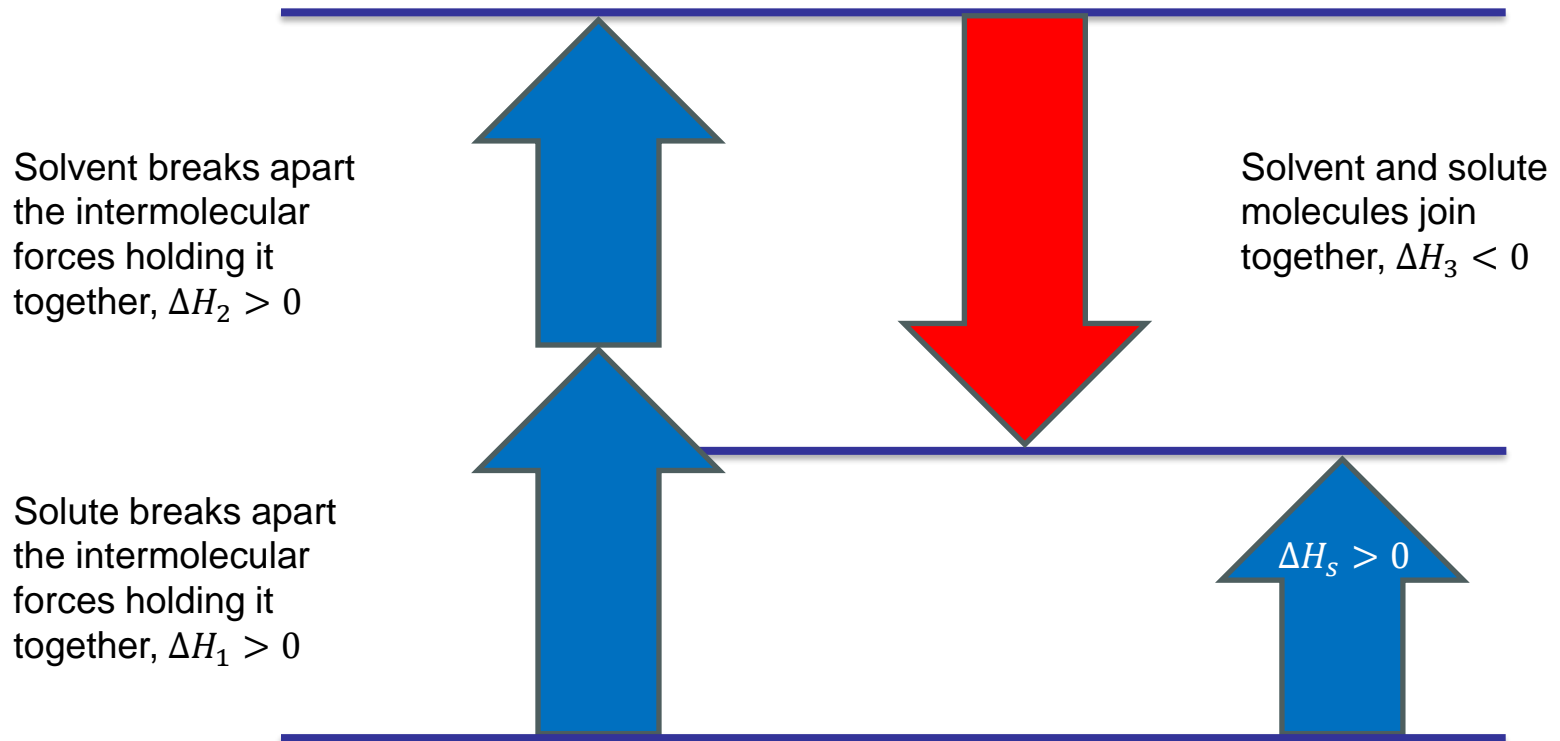


Fig.1 Energy diagram for endothermic dissolving process.

Hypothetical process

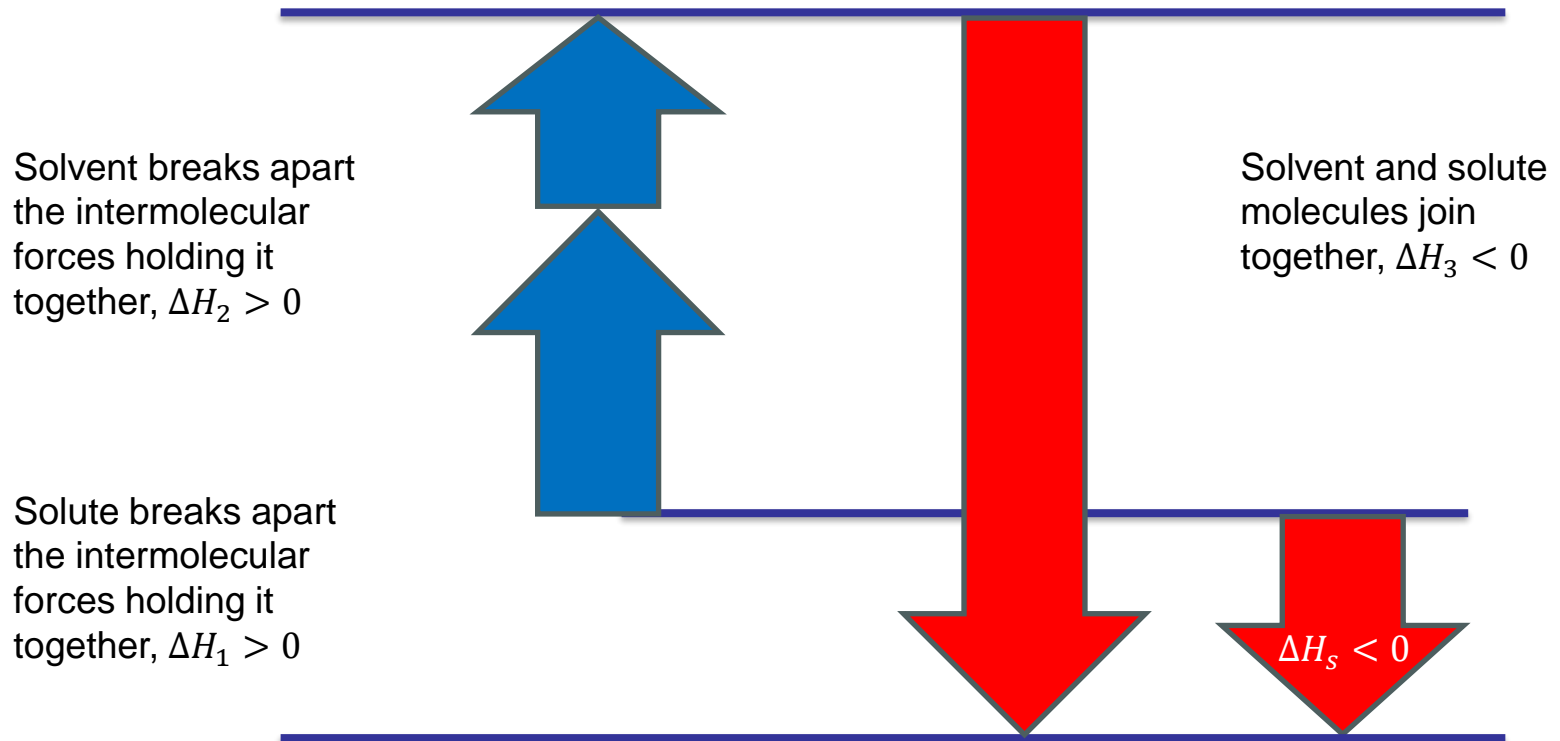


Fig.2 Energy diagram for exothermic dissolving process.

Hypothetical process

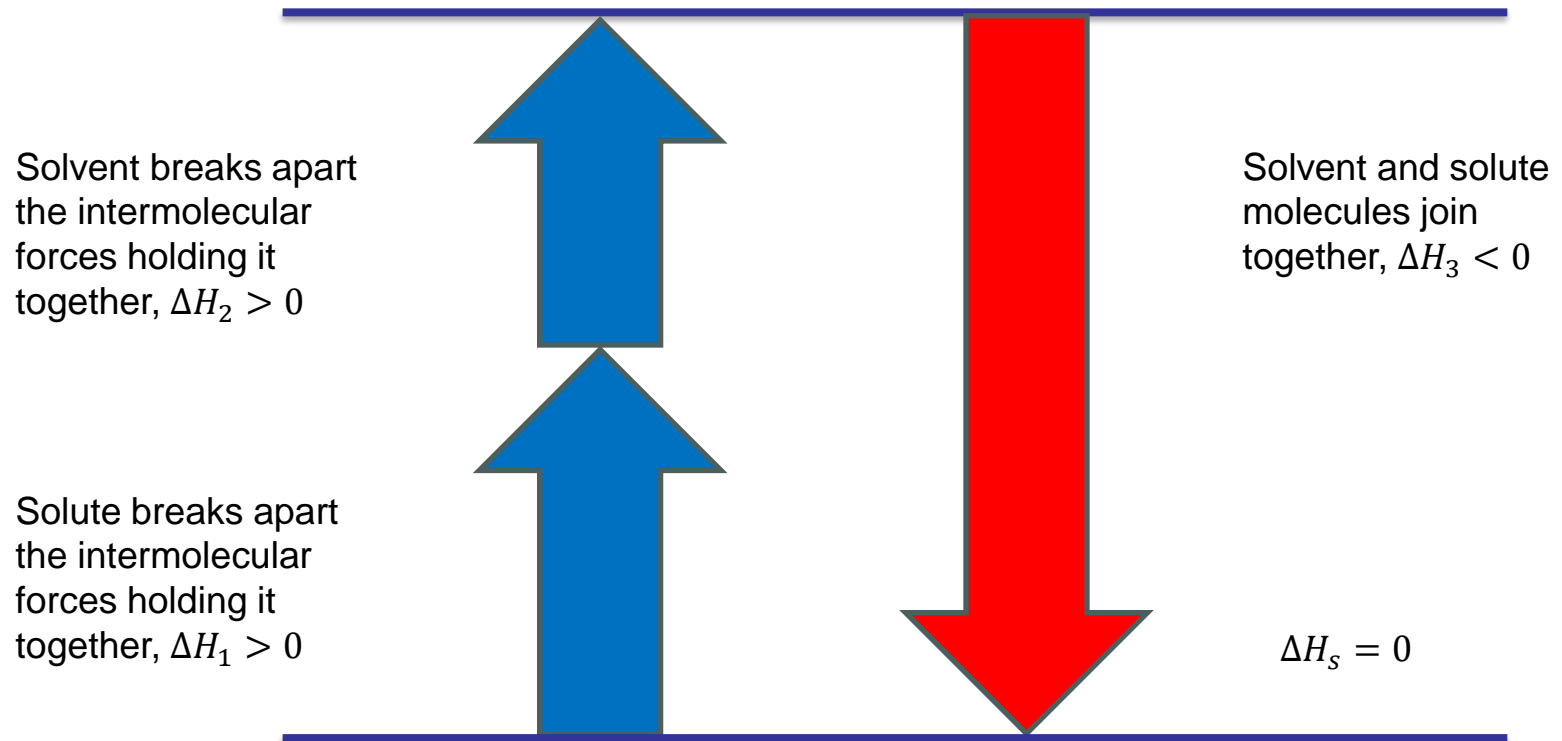


Fig.3 Energy diagram for an ideal dissolving process.

Ideal mixture

An **ideal mixture** is one for which the heat of mixing or solution is negligible and so

$$H_{mixture} = \sum n_i \hat{H}_i$$

where n_i is the amount of mixture component and \hat{H}_i is the specific enthalpy of the pure component at the temperature and pressure of the mixture.

The ideal-mixture assumption works well for nearly **all gas mixtures** and for **liquid mixtures of similar compounds** - such as mixtures of paraffins or of aromatics, but for other mixtures and solutions - such as aqueous solutions of strong acids or bases or certain gases (e.g., hydrogen chloride) or solids (e.g., sodium hydroxide) - heats of solution must be included in energy balance calculations.

Example 1

Calculate ΔH for a process in which 2 mol of potassium cyanide (KCN) is dissolved in 400 mol of water at 18°C.

Reference states

Heats of solution may be used to determine directly the specific enthalpies of solutions at 25°C relative to the **pure** solute and solvent at this temperature.

Another common choice of reference conditions, however, is the pure solvent and **an infinitely dilute solution** at 25°C.

Consider, for example, a hydrochloric acid solution

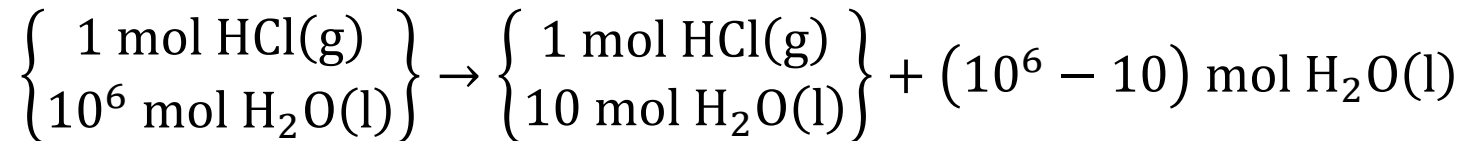
$$r = 10 \text{ mol H}_2\text{O/mol HCl}$$

From Table B.11,

$$\Delta \hat{H}_s(25^\circ\text{C}, r = 10) = -69.49 \text{ kJ/mol HCl}$$

Now, the enthalpy of the solution relative to $\text{H}_2\text{O(l)}$ and a highly dilute solution of HCl (say, $r = 10^6 \text{ mol H}_2\text{O/mol HCl}$) is the enthalpy change for the isothermal process:

Reference states



Taking **pure** HCl(g) and H₂O(l) at 25°C as references. \hat{H} for the $(10^6 - 10)$ moles of pure water equals zero, and the enthalpy change for the process is therefore

$$\begin{aligned} \Delta \hat{H} &= \Delta \hat{H}_s(25, r = 10) - \Delta \hat{H}_s(25, r = \infty) \\ &= (-69.49 + 75.14) = 5.65 \text{ kJ/mol HCl} \end{aligned}$$

For reference states of **pure solute and solvent** at 25°C and 1 atm, $\Delta \hat{H} = \Delta \hat{H}_s(T, r)$

For reference states of **pure solvent and an infinitely dilute solution** at 25°C and 1 atm, $\Delta \hat{H} = \Delta \hat{H}_s(T, r) - \Delta \hat{H}_s(T, \infty)$

Reference states

There are a few reasons for choosing an infinitely dilute solution as a reference state:

1. minimising interactions: at infinite dilution, the interactions between solute molecules are negligible. This allows for a more accurate assessment of the energy change associated with the solute dissolving in the solvent.
2. standard conditions: measuring the heat of solution at infinite dilution provides a standardised condition, which makes it easier to compare the thermodynamic properties of different solutes.
3. thermodynamic consistency: the heat of solution at infinite dilution can be related to other thermodynamic properties, such as enthalpy of mixing and Gibbs free energy of solvation, in a more straightforward way.

Test yourself

The heat of solution of a solute A in water at 25°C is -40 kJ/mol A for $r = 10 \text{ mol H}_2\text{O/mol A}$ and -60 kJ/mol A for infinite dilution.

1. what is the specific enthalpy in kJ/mol A of an aqueous solution of A for which $r = 10 \text{ mol H}_2\text{O/mol A}$ relative to
 - a. pure $\text{H}_2\text{O(l)}$ and A at 25°C?
 - b. pure $\text{H}_2\text{O(l)}$ and an infinitely dilute aqueous solution of A?
2. if 5 mol of A is dissolved in 50 mol of H_2O at 25°C, how much heat is evolved or absorbed?
3. how much heat is evolved or absorbed if the solution prepared in question 2 is poured into a large tank of water at 25°C?

Dissolution and mixing

When setting up an energy balance on a process that involves forming, concentrating, or diluting a solution for which the heat of solution or mixing cannot be neglected:

1. prepare an inlet-outlet enthalpy table considering the solution as a single substance and the pure components at 25°C as reference states.
2. calculate its enthalpy at 25°C from tabulated heat of solution data, then add the enthalpy change for the heating or cooling of the solution from 25°C to process temperature.
3. use tabulated solution heat capacities if they are available otherwise, use the average heat capacity determined for liquid mixtures or the heat capacity of the pure solvent for dilute solutions.

Example 2

Hydrochloric acid is produced by absorbing gaseous HCl (hydrogen chloride) in water. Calculate the heat that must be transferred to or from an absorption unit if HCl(g) at 100°C and H₂O(l) at 25°C are fed to produce 1000 kg/h of 20.0 wt% HCl(aq) at 40°C.

Perry's handbook

TABLE 2-164 Hydrochloric Acid

Mole % HCl	Specific heat, cal/(g·°C)				
	0 °C	10 °C	20 °C	40 °C	60 °C
0.0	1.00				
9.09	0.72	0.72	0.74	0.75	0.78
16.7	0.61	0.605	0.631	0.645	0.67
20.0	0.58	0.575	0.591	0.615	0.638
25.9	0.55				0.61