

Remember Δ means *final – initial* or *out – in*.

State Variable: Value depends only on location or “*state*.” Does not depend on path.

Common State Variables: $H, T, U, V, m, \text{etc.}$

Path Variable: Value depends only on path. Does not depend on location.

Common Path Variables: Q, W .

Problem: Calculate ΔH for one mole of ice at -5°C and 1 bar being changed to steam at 300°C and 5 bar.

Possible path:

1. Ice at -5°C and 1 bar to ice at 0°C and 1 bar
2. Ice at 0°C and 1 bar to water at 0°C and 1 bar
3. Water at 0°C and 1 bar to water at 100°C and 1 bar
4. Water at 100°C and 1 bar to steam at 100°C & 1 bar
5. Steam at 100°C & 1 bar to steam at 300°C and 1 bar
6. Steam at 300°C & 1 bar to steam at 300°C and 5 bar

For the process

$$\Delta \hat{H} = \sum_{i=1}^6 \Delta \hat{H}_i$$

Alternate path:

1. Ice at -5°C and 1 bar to ice at 0.01°C and 1 bar
2. Ice at 0.01°C and 1 bar to water at 0.01°C and 1 bar
3. Water at 0.01°C and 1 bar to steam at 300°C & 5 bar

For the process

$$\Delta\hat{H} = \sum_{i=1}^3 \Delta\hat{H}_i$$

Are the two equal?

Why or why not?

For many chemical engineering processes, work, kinetic energy, and potential energy can be ignored. In such cases the 1st law reduces to:

$$Q = \Delta U \quad (\text{Closed System})$$

$$\dot{Q} = \Delta \dot{H} \quad (\text{Open System})$$

For a constant volume system we define:

$$C_v(T) \equiv \lim_{\Delta T \rightarrow 0} \frac{\Delta \hat{U}}{\Delta T} = \frac{d\hat{U}}{dT}$$

C_v is the heat capacity at constant volume.

Rearranging

$$d\hat{U} = C_v(T)dT$$

and integrating

$$\Delta \hat{U} = \int_{T_1}^{T_2} C_v(T)dT$$

If C_v does not depend on T , then:

$$\Delta \hat{U} = C_v \Delta T$$

What if the volume changes?

For a constant pressure system we define:

$$C_p(T) \equiv \lim_{\Delta T \rightarrow 0} \frac{\Delta \hat{H}}{\Delta T} = \frac{d\hat{H}}{dT}$$

as before

$$d\hat{H} = C_p(T)dT$$

and

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T)dT$$

If C_p does not depend on T , then:

$$\Delta \hat{H} = C_p \Delta T$$

What if the pressure changes?

Ideal Gas:

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T) dT$$

Liquids and Solids

$$\begin{aligned} \Delta \hat{H} &= \int_{T_1}^{T_2} C_p(T) dT + \int_{P_1}^{P_2} \hat{V} dP \\ &\approx \int_{T_1}^{T_2} C_p(T) dT + \hat{V} \Delta P \end{aligned}$$

How do C_p and C_v compare?

Liquids and Solids:	$C_p \approx C_v$
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Ideal Gases:	$C_p = C_v + R$
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How do you evaluate heat capacities?

- Tables
- Correlations

From *Felder* (Table B.2 in appendix B)

$$C_p = a + bT + cT^2 + dT^3$$

or

$$C_p = a + bT + cT^{-2}$$

- Estimating formulas

If you know the initial and final temperatures, it is often convenient to use a mean heat capacity.

Definition:

$$\bar{C}_p = \frac{\hat{H}_2 - \hat{H}_1}{T_2 - T_1}$$

Evaluation: If you have a correlation from *Felder*,

$$\bar{C}_p = \frac{\int_{T_1}^{T_2} (a + bT + cT^2 + dT^3) dT}{T_2 - T_1}$$

which evaluates to

$$\begin{aligned}\bar{C}_p = & a + \frac{b}{2}(T_1 + T_2) + \frac{c}{3}(T_1^2 + T_1T_2 + T_2^2) \\ & + \frac{d}{4}[(T_1 + T_2)(T_1^2 + T_2^2)]\end{aligned}$$

Or

$$\bar{C}_P = \frac{\int_{T_1}^{T_2} (a + bT + cT^{-2}) dT}{T_2 - T_1}$$

which evaluates to

$$\bar{C}_P = a + \frac{b}{2}(T_1 + T_2) + \frac{c}{T_1T_2}$$

If you have tabulated heat capacities the integration can be done numerically.

It should be obvious that $\Delta\hat{H} = \bar{C}_p\Delta T$

Estimating formulas

If the tabulated data are missing use a formula like Kopp's Rule

$$(C_p)_{\text{compound}} = \sum_{\text{all atoms}} C_{pa}$$

Atomic Heat-Capacity Contributions for Kopp's Rule		
C_{pa} (J/g-atom °C)		
Element	Solids	Liquids
C	7.5	12
H	9.6	18
B	11	20
Si	16	24
O	17	25
F	21	29
P	23	31
S	26	31
All others	26	33

How about mixtures?

Lacking other data, use a weighted average.

The $C_p \Delta T$ changes are known as *sensible heat changes*. During a phase change heat is added without a change in temperature. Such changes are *latent heat changes*.

- Latent heat of vaporization, $\Delta \hat{H}_v$
- Latent heat of fusion, $\Delta \hat{H}_m$
- Latent heat of sublimation, $\Delta \hat{H}_s$

Why ΔH ? Why not ΔU ?

Vaporize one pound of water at constant T and P .

What kind of system?

The 1st law is:

$$\Delta U = Q - W$$

For a closed system the pressure-volume work is:

$$W = \int P dV$$

Now if $P = \text{constant}$

$$W = P\Delta V = \Delta(PV)$$

So the 1st law becomes:

$$\Delta U = Q - \Delta(PV)$$

or

$$\Delta U + \Delta(PV) = \Delta H = Q$$

The book lies a little.

How do you evaluate latent heats?

- Tables
- Correlations
- Educated Guesses

Trouton's Rule (within 30% accuracy)

nonpolar liquids

$$(\Delta\hat{H}_v)_{\text{nbp}}[\text{kJ/mol}] \approx 0.088T_b(\text{K})$$

water, low-MW alcohols

$$(\Delta\hat{H}_v)_{\text{nbp}}[\text{kJ/mol}] \approx 0.109T_b(\text{K})$$

Chen's equation (within 2% accuracy)

$$(\Delta\hat{H}_v)_{\text{nbp}}[\text{kJ/mol}] = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297\log_{10}P_c]}{1.07 - (T_b/T_c)}$$

with T 's in Kelvin, P in atm., and $\Delta\hat{H}$ in kJ/mol

Also **Chapter 6 backwards**

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R}$$

And finally the **Watson correlation**

$$\frac{\Delta\hat{H}_v(T_2)}{\Delta\hat{H}_v(T_1)} = \left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$

Page 381's Rule (??% accurate)

For metallic elements

$$\Delta\hat{H}_m \approx 0.0092T_m(\text{K})$$

For inorganic compounds

$$\Delta\hat{H}_m \approx 0.025T_m(\text{K})$$

For organic compounds

$$\Delta\hat{H}_m \approx 0.05T_m(\text{K})$$

Psychrometric Chart

Find:

- Humid Volume
- Dry Bulb Temperature
- Wet Bulb Temperature

(Note, the wet bulb temperature is *not* the dew point temperature.)

- Absolute Humidity
- Relative Humidity
- Enthalpy
- Enthalpy Deviation
- Adiabatic Saturation Line

Example: You set out a cold (root)brew on a day when the temperature is 86°F and the relative humidity is 30%. At what temperature is the brew when water quits condensing on the can? (squid questions: What is the dew point? What is the wet bulb temperature? What is the absolute humidity? What is the specific volume? What is the enthalpy relative to liquid water and dry air at 0°C ?)

Example: Hot Air at 43°C and 10% relative humidity enters an adiabatic clothes dryer containing 5 kg of water (and assorted clothes) and exits at 90% relative humidity. How many cubic meters of air are required to completely dry the clothes? What is the steady-state temperature of the exiting air? Of the clothes?

Reference states

Calculate the average heat capacity of saturated steam from 10°C to 90°C for both of the steam tables given below:

	$\hat{H}(\text{kJ/kg})$	$\hat{H}(\text{kJ/kg})$
$T(^{\circ}\text{C})$	water	steam
0	0.0	2501.6
10	42.0	2519.9
20	83.9	2538.2
30	125.7	2556.4
40	167.5	2574.4
50	209.3	2592.2
60	251.1	2609
70	293.0	2626
80	334.9	2643
90	377.0	2659
100	419.1	2676

	$\hat{H}(\text{kJ/kg})$	$\hat{H}(\text{kJ/kg})$
$T(^{\circ}\text{C})$	water	steam
0	-2676.0	-174.4
10	-2634.0	-156.1
20	-2592.1	-137.8
30	-2550.3	-119.6
40	-2508.5	-101.6
50	-2466.7	-83.8
60	-2424.9	-67
70	-2383.0	-50
80	-2341.1	-33
90	-2299.0	-17
100	-2256.9	0

Table 1

$$\bar{C}_p = \frac{\hat{H}_2 - \hat{H}_1}{T_2 - T_1} = \frac{2659 - 2519.9}{90 - 10} = 1.739 \frac{\text{kJ}}{\text{kg}^\circ\text{C}}$$

Table 2

$$\bar{C}_p = \frac{\hat{H}_2 - \hat{H}_1}{T_2 - T_1} = \frac{-17 - (-156.1)}{90 - 10} = 1.739 \frac{\text{kJ}}{\text{kg}^\circ\text{C}}$$

Why are the tables different?

(Specific) Integral Heat of Solution

$$\Delta\hat{H}_s(T, n)$$

One mole of solute dissolved in n moles of solvent.

Usually referenced to pure solvent at some T . Can be referenced to pure solute *or* infinitely dilute solute

(Specific) Integral Heat of Mixing

One mole of solution made from x moles of liquid 1 and $1 - x$ moles of liquid 2. Usually referenced to pure species 1 and species 2 at some temperature.

Example: A 30% solution of NaOH in water at 100°F is to be diluted to a 10% solution by adding pure water. What temperature must the dilution water be at for the final mixture to be at 80°F.

Example: A 50% H_2O –50% NH_3 mixture at its bubble point is introduced into a heated single-stage flash unit. The exit streams are at 120°F. What are their compositions and how much heat must be added to the flash per pound of feed?

Valuable Numbers to Know

Approximate Heat Capacities

Gas Type	C_v	C_p
Monatomic	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic	$\frac{5}{2}R$	$\frac{7}{2}R$

Water Values

$$C_p \left[\frac{\text{BTU}}{\text{lb}_m \text{ } ^\circ\text{F}} \right] \text{ or } \left[\frac{\text{cal}}{\text{g } ^\circ\text{C}} \right]$$

$$\text{Steam} \approx 0.5$$

$$\text{Water} \approx 1.0$$

$$\text{Ice} \approx 0.5$$

$$\Delta \hat{H}_v \approx 1000 \left[\frac{\text{BTU}}{\text{lb}_m \text{ } ^\circ\text{F}} \right]$$

$$\Delta \hat{H}_m \approx 150 \left[\frac{\text{BTU}}{\text{lb}_m \text{ } ^\circ\text{F}} \right]$$