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E82

ΔU and ΔH as Functions of Temperature and Pressure

E82 – What to do if your temperature or pressure isn't constant

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

State Variable: Value depends only on location or "*state*." Does no depend on path.

Common State Variables: H, T, U, V, m, etc.

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

Common Path Variables: Q, W.

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Example: Calculate ΔH for one mole of ice at –5°C and 1 atm being changed to steam at 300°C and 5 bar by two different paths.

Path 1 :

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

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

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Path 2:

1. Ice at –5°C and 1 atm to ice at 0.01°C and 0.00611 bar
2. Ice at 0.01°C and 0.00611 bar to water at 0.01°C and 0.00611 bar
3. Water at 0.01°C and 0.00611 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?

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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:

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

C_v is the *heat capacity* at *constant volume*.

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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?

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For a constant pressure system we define:

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

C_p is the *heat capacity* at *constant pressure*. As before

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

and integrating

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

If C_p does not depend on T, then:

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

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What if the pressure changes?

In general:

$$d\hat{H} = C_p dT + \left[\hat{V} - T\left(\frac{\partial \hat{V}}{\partial T}\right)_P\right]dP$$

Ideal Gas:

$$\Delta \hat{H} = \int_{T_1}^{T_2} C_p(T)dT \qquad \text{No pressure dependence}$$

Liquids and Solids:

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

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How do C_p and C_v compare?

Ideal Gas: $C_p = C_v + R$

Liquids and Solids: $C_v \approx C_p$

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.

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Definition:

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

Evaluation (Form 1):

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

which evaluates to

$$\bar{C}_p = a + \frac{b}{2}\left(T_1 + T_2\right) + \frac{c}{3}\left(T_1^2 + T_1 T_2 + T_2^2\right) + \frac{d}{4}\left[\left(T_1 + T_2\right)\left(T_1^2 + T_2^2\right)\right]$$

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Evaluation (Form 2):

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

which evaluates to

$$\bar{C}_p = a + \frac{b}{2}\left(T_1 + T_2\right) + \frac{c}{T_1 T_2}$$

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

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It should be obvious that

$$\Delta\hat{H} = \bar{C}_p \Delta T$$

but things in thermodynamics rarely are.

If you have not already done so, you should also do the symbolic integration of the correlations for

$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT = \int_{T_1}^{T_2}\left(a + bT + cT^2 + dT^3\right)dT \quad \text{or} \quad = \int_{T_1}^{T_2}\left(a + bT + cT^{-2}\right)dT$$

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Example: Calculate ΔH for 10 moles of N_2 going from 100°C to 800°C. Compare the results for an approximate heat capacity, the mean heat capacity formula, integrating the heat capacity, and using Table B.8 in FRB.

Approximate heat capacity for a diatomic gas.

$$C_p = \frac{7}{2}R = 3.5 \bullet 8.314\frac{\text{J}}{\text{mol K}} = 29.10\frac{\text{J}}{\text{mol K}} = 0.0291\frac{\text{kJ}}{\text{mol K}}$$

$$\Delta\hat{H} = C_p\Delta T = 0.0291\left(800 - 100\right) = 20.37 \text{ kJ/mol}$$

$$\Delta H = n\Delta\hat{H} = 10 \bullet 20.37 \text{ kJ/mol} = 203.7 \text{ kJ}$$

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Mean heat capacity from Table B.2 in FRB

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$$\bar{C}_p = a + \frac{b}{2}\left(T_1 + T_2\right) + \frac{c}{3}\left(T_1^2 + T_1 T_2 + T_2^2\right) + \frac{d}{4}\left[\left(T_1 + T_2\right)\left(T_1^2 + T_2^2\right)\right]$$

$$a = 29.00\times10^{-3},\ b = 0.2199\times10^{-5},\ c = 0.5723\times10^{-8},\ d = -2.871\times10^{-12}$$

$$\bar{C}_p = 30.96\,\frac{\text{J}}{\text{mol K}} = 0.03096\,\frac{\text{kJ}}{\text{mol K}}$$

$$\Delta\hat{H} = \bar{C}_p\Delta T = 0.03096\left(800 - 100\right) = 21.67\ \text{kJ/mol}$$

$$\Delta H = n\Delta\hat{H} = 10 \bullet 21.67\ \text{kJ/mol} = 216.7\ \text{kJ}$$

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Integrating heat capacity from Table B.2 in FRB

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$$\Delta\hat{H} = \int_{T_1}^{T_2} C_p(T)\,dT = \int_{T_1}^{T_2}\left(a + bT + cT^2 + dT^3\right)dT$$

$$a = 29.00\times10^{-3},\ b = 0.2199\times10^{-5},\ c = 0.5723\times10^{-8},\ d = -2.871\times10^{-12}$$

$$\Delta\hat{H} = 21.67\ \text{kJ/mol}$$

$$\Delta H = n\Delta\hat{H} = 10 \bullet 21.67\ \text{kJ/mol} = 216.7\ \text{kJ}$$

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Calculating from enthalpies from Table B.8 in FRB

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$$@100\ °C,\ \hat{H} = 2.19\ \text{kJ/mol}$$

$$@800\ °C,\ \hat{H} = 23.86\ \text{kJ/mol}$$

$$\Delta\hat{H} = \hat{H}_{800} - \hat{H}_{100} = 23.86 - 2.19 = 21.67\ \text{kJ/mol}$$

$$\Delta H = n\Delta\hat{H} = 10 \bullet 21.67\ \text{kJ/mol} = 216.7\ \text{kJ}$$

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R	8.3145	J/mol K		Comparison	C_p	ΔHhat	ΔH	% diff
n	10	g-mol		Approx C_p	0.02910	20.37	203.7	-6.01%
T_1	100	°C		Mean C_p	0.03096	21.67	216.7	0.00%
T_2	800	°C		Int. C_p	N/A	21.67	216.7	0.00%
				Table B.8	N/A	21.67	216.7	-0.02%
7/2 R	0.02910	kJ/mol K						
ΔHhat	20.37	kJ/mol						
ΔH	**203.7**	**kJ**						
$C_p$bar	0.03096	kJ/mol °C	a	b	c	d		
ΔHhat	21.67	kJ/mol	2.90E-02	2.20E-06	5.72E-09	-2.87E-12		
ΔH	**216.7**	**kJ**						
ΔHhat	21.67	kJ/mol						
ΔH	**216.7**	**kJ**						
	Hhat (kJ/mol)							
100 °C	2.19							
800 °C	23.86							
ΔHhat	21.67	kJ/mol						
ΔH	**216.7**	**kJ**						

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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

$$C_p\left[\frac{\text{Btu}}{\text{lb}_\text{m}\ {}^\circ\text{F}}\right] \text{ or } \left[\frac{\text{cal}}{\text{g}\ {}^\circ\text{C}}\right]$$

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

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

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

$$\Delta\hat{H}_v \approx 1000\left[\frac{\text{Btu}}{\text{lb}_\text{m}}\right]$$

$$\Delta\hat{H}_m \approx 150\left[\frac{\text{Btu}}{\text{lb}_\text{m}}\right]$$

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