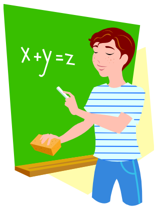
Reflection

After Action Report

What did I learn from this HW assignment?

Class 27

Enthalpies,
Heat Capacities
Heats of Formation,
Oh My!



Review of Energy Balances

$$\Delta\dot{H} + \Delta\dot{E}_K + \Delta\dot{E}_P = \dot{Q} + \dot{W}_s$$

- Enthalpies needed to calculate heat or work terms
- Methods to calculate enthalpy (so far):
  - Steam tables
  - Graph (P-H diagram)
  - Interpolation from 2 given values
- Needed: Method to get enthalpies for any species as a function of T & P

We Can't Measure Enthalpy!

Things we can measure:

- T, $y_{i,}$ P, Q, W_s
- Last HW assignment had you fit H vs T

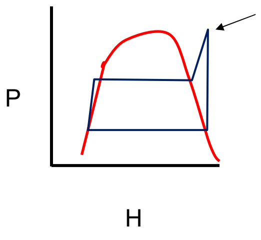
$$\hat{H} = mT + b$$

- Today we will find a way to get $\hat{H}$ for any species at any temperature.
- Idea: Measure Q, find $\Delta\hat{H}$

Concepts

1. Enthalpy is a state function
2. Heat Capacities
3. Latent Heats (phase change)
4. Heat of Formation
5. Calculating ΔH as *f*(T,P)

Concept 1.
Enthalpy Is A State Function



Rankine cycle
(most common method to
generate electricity!)

H is the same here regardless of path

- Enthalpy is independent of path
- Always talk about ΔH from some reference condition
  - Steam tables: $\hat{H} = 0$ at triple point
  - Other tables are different (e.g., in Table B.1,$\Delta\hat{H}_f^o$ for H_2 = 0 at 25°C)
  - Don't mix and match tables!!!

Concept 2.
Heat Capacities

- $\hat{H} = f(T,P)$ $\quad$ $d\hat{H} = \left(\frac{\partial \hat{H}}{\partial T}\right)_P dT + \boxed{\left(\frac{\partial \hat{H}}{\partial P}\right)_T dP}$
- $\hat{U} = f(T,\hat{V})$ $\quad$ $d\hat{U} = \left(\frac{\partial \hat{U}}{\partial T}\right)_V dT + \boxed{\left(\frac{\partial \hat{U}}{\partial \hat{V}}\right)_T d\hat{V}}$

Generally small

- Now define heat capacities:

$$\boxed{C_P = \left(\frac{\partial \hat{H}}{\partial T}\right)_P, \quad C_V = \left(\frac{\partial \hat{U}}{\partial T}\right)_V}$$

- For ideal gases:

$$d\hat{H} \equiv C_P dT, \qquad d\hat{U} \equiv C_V dT$$

- For solids and liquids:

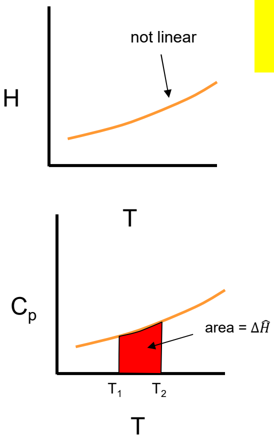
$$d\hat{H} = C_P dT + \hat{V} dP$$

Not small

- For non-ideal gases:

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

Concept 2.
Heat Capacities (cont.)



- $C_P = \left(\frac{\partial \hat{H}}{\partial T}\right)_P$ (like slope of H vs T curve, prob 7.55)
- $\Delta\hat{H} = \int_{T_1}^{T_2} C_P \, dT$
- $C_P = a + bT + cT^2 + dT^3 + \cdots$
- so

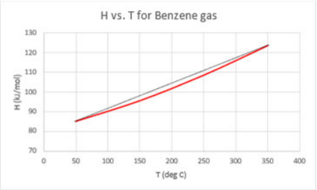
$$\Delta\hat{H}_{T_1\to T_2} = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3)\, dT$$

$$= a(T_2 - T_1) + \frac{b}{2}({T_2}^2 - {T_1}^2) + \frac{c}{3}({T_2}^3 - {T_1}^3) + \frac{d}{4}({T_2}^4 - {T_1}^4)$$

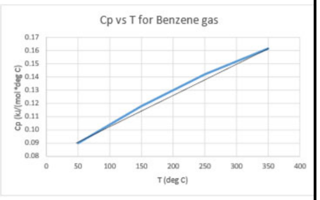
- For ideal gases: $C_p = C_v + R$
- For solids and liquids, $C_P \cong C_V$

A Practical View

- Wouldn't it be nice to have a polynomial equation for H!
- H = a + bT + cT^2


H vs. T for Benzene gas

- This would not work for different reference enthalpies!
- Solution: Polynomial for C_p
  - $C_P = a + bT + cT^2 + dT^3$ (= dH/dT)
  - Fit to thermodynamic data
  - $\Delta\widehat{H}_{T_1 \to T_2} = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3)\, dT$


Cp vs T for Benzene gas

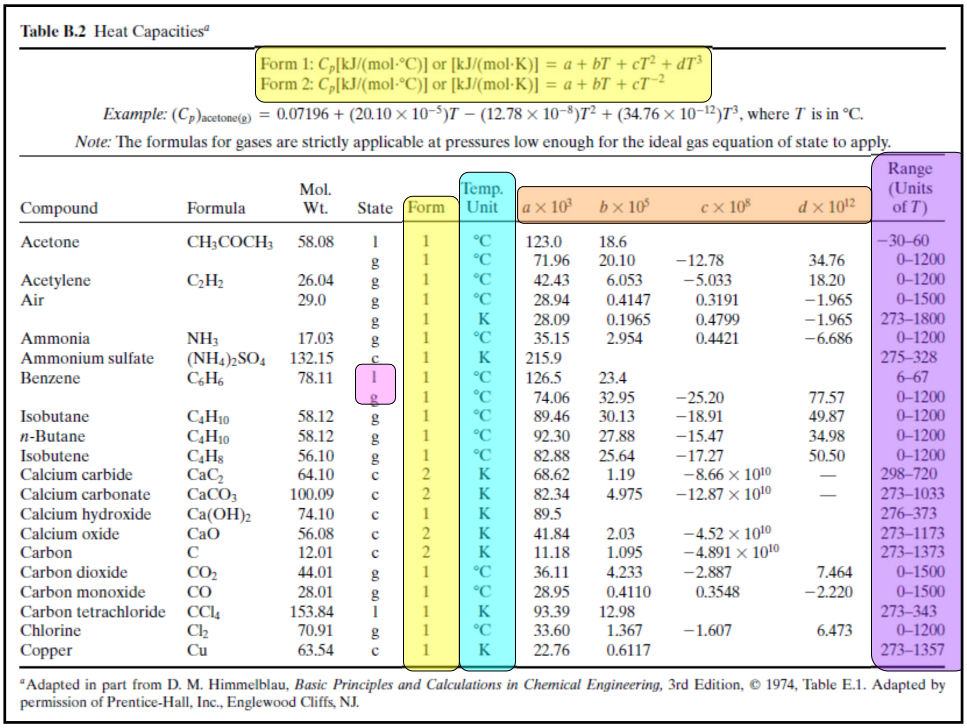


Table B.2 Heat Capacities[a]

Form 1: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] = $a + bT + cT^2 + dT^3$
Form 2: C_p[kJ/(mol·°C)] or [kJ/(mol·K)] = $a + bT + cT^{-2}$

Example: $(C_p)_{\text{acetone(g)}} = 0.07196 + (20.10 \times 10^{-5})T - (12.78 \times 10^{-8})T^2 + (34.76 \times 10^{-12})T^3$, where T is in °C.

Note: The formulas for gases are strictly applicable at pressures low enough for the ideal gas equation of state to apply.

Compound	Formula	Mol. Wt.	State	Form	Temp. Unit	$a \times 10^3$	$b \times 10^5$	$c \times 10^8$	$d \times 10^{12}$	Range (Units of T)
Acetone	CH_3COCH_3	58.08	l	1	°C	123.0	18.6			−30–60
			g	1	°C	71.96	20.10	−12.78	34.76	0–1200
Acetylene	C_2H_2	26.04	g	1	°C	42.43	6.053	−5.033	18.20	0–1200
Air		29.0	g	1	°C	28.94	0.4147	0.3191	−1.965	0–1500
			g	1	K	28.09	0.1965	0.4799	−1.965	273–1800
Ammonia	NH_3	17.03	g	1	°C	35.15	2.954	0.4421	−6.686	0–1200
Ammonium sulfate	$(NH_4)_2SO_4$	132.15	c	1	K	215.9				275–328
Benzene	C_6H_6	78.11	l	1	°C	126.5	23.4			6–67
			g	1	°C	74.06	32.95	−25.20	77.57	0–1200
Isobutane	C_4H_{10}	58.12	g	1	°C	89.46	30.13	−18.91	49.87	0–1200
n-Butane	C_4H_{10}	58.12	g	1	°C	92.30	27.88	−15.47	34.98	0–1200
Isobutene	C_4H_8	56.10	g	1	°C	82.88	25.64	−17.27	50.50	0–1200
Calcium carbide	CaC_2	64.10	c	2	K	68.62	1.19	-8.66×10^{10}	—	298–720
Calcium carbonate	$CaCO_3$	100.09	c	2	K	82.34	4.975	-12.87×10^{10}	—	273–1033
Calcium hydroxide	$Ca(OH)_2$	74.10	c	1	K	89.5				276–373
Calcium oxide	CaO	56.08	c	2	K	41.84	2.03	-4.52×10^{10}		273–1173
Carbon	C	12.01	c	2	K	11.18	1.095	-4.891×10^{10}		273–1373
Carbon dioxide	CO_2	44.01	g	1	°C	36.11	4.233	−2.887	7.464	0–1500
Carbon monoxide	CO	28.01	g	1	°C	28.95	0.4110	0.3548	−2.220	0–1500
Carbon tetrachloride	CCl_4	153.84	l	1	K	93.39	12.98			273–343
Chlorine	Cl_2	70.91	g	1	°C	33.60	1.367	−1.607	6.473	0–1200
Copper	Cu	63.54	c	1	K	22.76	0.6117			273–1357

[a] Adapted in part from D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, © 1974, Table E.1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

Caution!

- When getting a heat capacity coefficient from Table B.2, use the multiplier at the top of the column
- Example: Acetone
  - a = 123
  - multiplier = 10^3
    (i.e., the actual number was multiplied by 10^3 to make it look nicer in the table)
  - Therefore, **$a = 123 \times 10^{-3}$ kJ/(gmol·K)**

DIPPR Format

$$C_p = A + B\left[\frac{C/T}{\sinh\left(C/T\right)}\right]^2 + D\left[\frac{E/T}{\cosh\left(E/T\right)}\right]^2$$

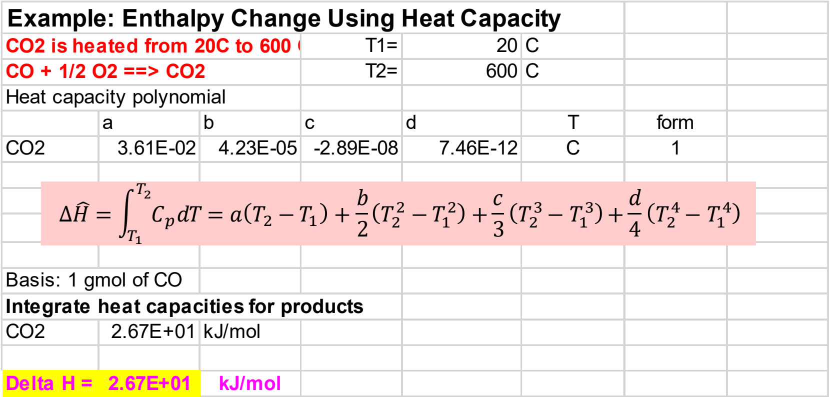
Integrated form:

$$\int_{T_1}^{T_2} C_p dT = A\left[T_2 - T_1\right] + BC\left[\coth\left(\frac{C}{T_2}\right) - \coth\left(\frac{C}{T_1}\right)\right] - DE\left[\tanh\left(\frac{E}{T_2}\right) - \tanh\left(\frac{E}{T_1}\right)\right]$$

Heat Capacity Example

Student volunteer needed!

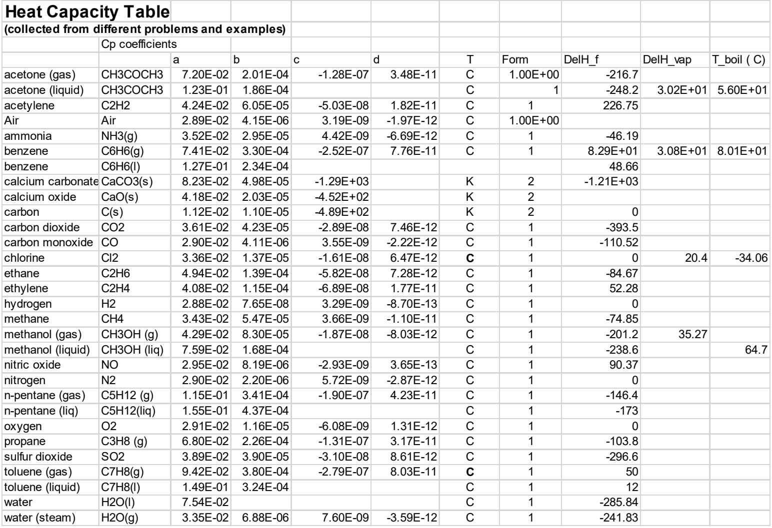
Heat Capacity Example



Example: Enthalpy Change Using Heat Capacity							
CO2 is heated from 20C to 600 (			T1=	20	C		
CO + 1/2 O2 ==> CO2			T2=	600	C		
Heat capacity polynomial							
	a	b	c	d	T	form	
CO2	3.61E-02	4.23E-05	-2.89E-08	7.46E-12	C	1	
Basis: 1 gmol of CO							
Integrate heat capacities for products							
CO2	2.67E+01	kJ/mol					
Delta H =	**2.67E+01**	**kJ/mol**					

$$\Delta\hat{H}=\int_{T_1}^{T_2}C_p\,dT=a(T_2-T_1)+\frac{b}{2}(T_2^2-T_1^2)+\frac{c}{3}(T_2^3-T_1^3)+\frac{d}{4}(T_2^4-T_1^4)$$

I put an excel sheet with the heat capacity coefficients on the class web page



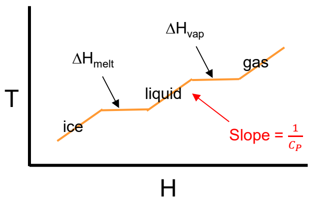
Heat Capacity Table										
(collected from different problems and examples)										
	Cp coefficients									
		a	b	c	d	T	Form	DelH_f	DelH_vap	T_boil (C)
acetone (gas)	CH3COCH3	7.20E-02	2.01E-04	-1.28E-07	3.48E-11	C	1.00E+00	-216.7		
acetone (liquid)	CH3COCH3	1.23E-01	1.86E-04			C	1	-248.2	3.02E+01	5.60E+01
acetylene	C2H2	4.24E-02	6.05E-05	-5.03E-08	1.82E-11	C	1	226.75		
Air	Air	2.89E-02	4.15E-06	3.19E-09	-1.97E-12	C	1.00E+00			
ammonia	NH3(g)	3.52E-02	2.95E-05	4.42E-09	-6.69E-12	C	1	-46.19		
benzene	C6H6(g)	7.41E-02	3.30E-04	-2.52E-07	7.76E-11	C	1	8.29E+01	3.08E+01	8.01E+01
benzene	C6H6(l)	1.27E-01	2.34E-04					48.66		
calcium carbonate	CaCO3(s)	8.23E-02	4.98E-05	-1.29E+03		K	2	-1.21E+03		
calcium oxide	CaO(s)	4.18E-02	2.03E-05	-4.52E+02		K	2			
carbon	C(s)	1.12E-02	1.10E-05	-4.89E+02		K	2	0		
carbon dioxide	CO2	3.61E-02	4.23E-05	-2.89E-08	7.46E-12	C	1	-393.5		
carbon monoxide	CO	2.90E-02	4.11E-06	3.55E-09	-2.22E-12	C	1	-110.52		
chlorine	Cl2	3.36E-02	1.37E-05	-1.61E-08	6.47E-12	**C**	1	0	20.4	-34.06
ethane	C2H6	4.94E-02	1.39E-04	-5.82E-08	7.28E-12	C	1	-84.67		
ethylene	C2H4	4.08E-02	1.15E-04	-6.89E-08	1.77E-11	C	1	52.28		
hydrogen	H2	2.88E-02	7.65E-08	3.29E-09	-8.70E-13	C	1	0		
methane	CH4	3.43E-02	5.47E-05	3.66E-09	-1.10E-11	C	1	-74.85		
methanol (gas)	CH3OH (g)	4.29E-02	8.30E-05	-1.87E-08	-8.03E-12	C	1	-201.2	35.27	
methanol (liquid)	CH3OH (liq)	7.59E-02	1.68E-04			C	1	-238.6		64.7
nitric oxide	NO	2.95E-02	8.19E-06	-2.93E-09	3.65E-13	C	1	90.37		
nitrogen	N2	2.90E-02	2.20E-06	5.72E-09	-2.87E-12	C	1	0		
n-pentane (gas)	C5H12 (g)	1.15E-01	3.41E-04	-1.90E-07	4.23E-11	C	1	-146.4		
n-pentane (liq)	C5H12(liq)	1.55E-01	4.37E-04			C	1	-173		
oxygen	O2	2.91E-02	1.16E-05	-6.08E-09	1.31E-12	C	1	0		
propane	C3H8 (g)	6.80E-02	2.26E-04	-1.31E-07	3.17E-11	C	1	-103.8		
sulfur dioxide	SO2	3.89E-02	3.90E-05	-3.10E-08	8.61E-12	C	1	-296.6		
toluene (gas)	C7H8(g)	9.42E-02	3.80E-04	-2.79E-07	8.03E-11	**C**	1	50		
toluene (liquid)	C7H8(l)	1.49E-01	3.24E-04			C	1	12		
water	H2O(l)	7.54E-02				C	1	-285.84		
water (steam)	H2O(g)	3.35E-02	6.88E-06	7.60E-09	-3.59E-12	C	1	-241.83		

Concepts

1. Enthalpy is a state function
2. Heat Capacities
3. Latent Heats (phase change)
4. Heat of Formation
5. Calculating ΔH as *f*(T,P)

Concept 3.

Phase Changes (pure substances)



$$\Delta\hat{H}_{melt} = \hat{H}_{liq} - \hat{H}_{solid} \quad \text{(tabulated)}$$

$$\Delta\hat{H}_{vap} = \hat{H}_{gas} - \hat{H}_{liq} \quad \text{(tabulated)}$$

$$\Delta\hat{H}_{freezing} = -\Delta\hat{H}_{melt}$$

$$\Delta\hat{H}_{condens} = -\Delta\hat{H}_{vap}$$

Also we could find $\Delta\hat{H}_{sub}$

Remember that for a pure substance, T is constant during a phase change

- The heat of phase change is called **latent heat**, which comes from the fact that the temperature does not change during phase change
- The heat required to merely change the temperature of a substance is called the **sensible heat**

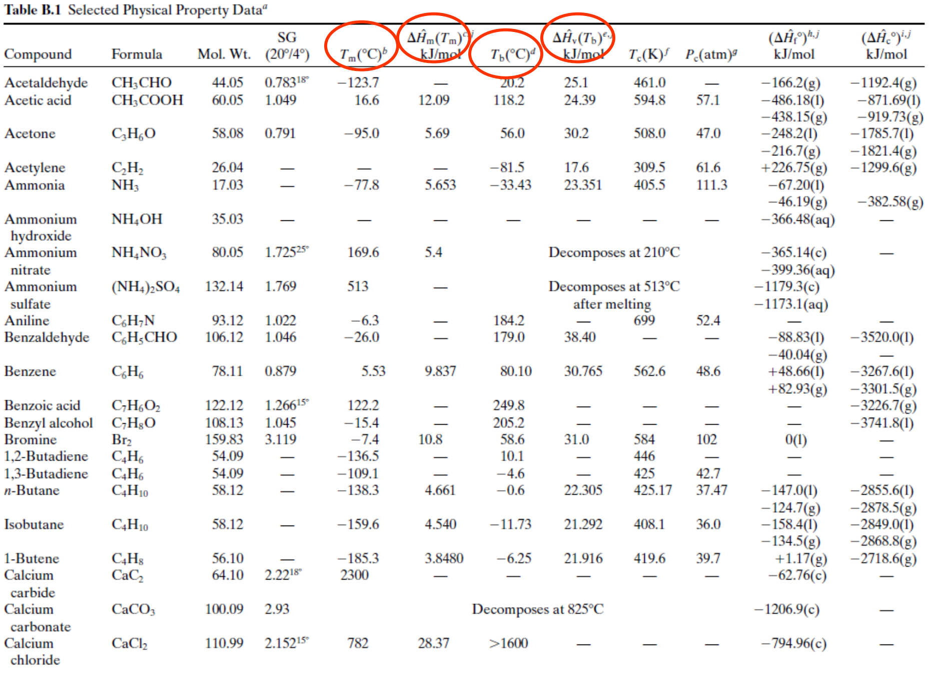
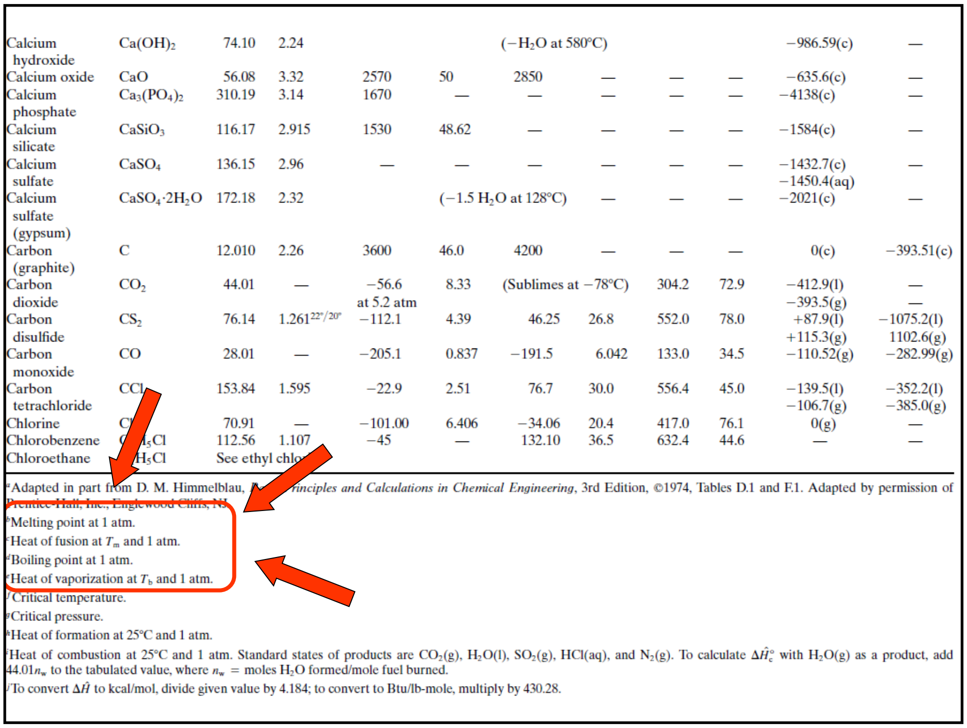


Table B.1 Selected Physical Property Data[a]

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)$[c,j] kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)$[e,j] kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f^\circ)$[h,j] kJ/mol	$(\Delta\hat{H}_c^\circ)$[i,j] kJ/mol
Acetaldehyde	CH_3CHO	44.05	0.783^18°	−123.7	—	20.2	25.1	461.0	—	−166.2(g)	−1192.4(g)
Acetic acid	CH_3COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	−486.18(l) −438.15(g)	−871.69(l) −919.73(g)
Acetone	C_3H_6O	58.08	0.791	−95.0	5.69	56.0	30.2	508.0	47.0	−248.2(l) −216.7(g)	−1785.7(l) −1821.4(g)
Acetylene	C_2H_2	26.04	—	—	—	−81.5	17.6	309.5	61.6	+226.75(g)	−1299.6(g)
Ammonia	NH_3	17.03	—	−77.8	5.653	−33.43	23.351	405.5	111.3	−67.20(l) −46.19(g)	−382.58(g)
Ammonium hydroxide	NH_4OH	35.03	—	—	—	—	—	—	—	−366.48(aq)	—
Ammonium nitrate	NH_4NO_3	80.05	1.725^25°	169.6	5.4	Decomposes at 210°C				−365.14(c) −399.36(aq)	—
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	1.769	513	—	Decomposes at 513°C after melting				−1179.3(c) −1173.1(aq)	
Aniline	C_6H_7N	93.12	1.022	−6.3	—	184.2	—	699	52.4	—	—
Benzaldehyde	C_6H_5CHO	106.12	1.046	−26.0	—	179.0	38.40	—	—	−88.83(l) −40.04(g)	−3520.0(l) —
Benzene	C_6H_6	78.11	0.879	5.53	9.837	80.10	30.765	562.6	48.6	+48.66(l) +82.93(g)	−3267.6(l) −3301.5(g)
Benzoic acid	$C_7H_6O_2$	122.12	1.266^15°	122.2	—	249.8	—	—	—	—	−3226.7(g)
Benzyl alcohol	C_7H_8O	108.13	1.045	−15.4	—	205.2	—	—	—	—	−3741.8(l)
Bromine	Br_2	159.83	3.119	−7.4	10.8	58.6	31.0	584	102	0(l)	—
1,2-Butadiene	C_4H_6	54.09	—	−136.5	—	10.1	—	446	—	—	—
1,3-Butadiene	C_4H_6	54.09	—	−109.1	—	−4.6	—	425	42.7	—	—
n-Butane	C_4H_{10}	58.12	—	−138.3	4.661	−0.6	22.305	425.17	37.47	−147.0(l) −124.7(g)	−2855.6(l) −2878.5(g)
Isobutane	C_4H_{10}	58.12	—	−159.6	4.540	−11.73	21.292	408.1	36.0	−158.4(l) −134.5(g)	−2849.0(l) −2868.8(g)
1-Butene	C_4H_8	56.10	—	−185.3	3.8480	−6.25	21.916	419.6	39.7	+1.17(g)	−2718.6(g)
Calcium carbide	CaC_2	64.10	2.22^18°	2300	—	—	—	—	—	−62.76(c)	—
Calcium carbonate	$CaCO_3$	100.09	2.93			Decomposes at 825°C				−1206.9(c)	—
Calcium chloride	$CaCl_2$	110.99	2.152^15°	782	28.37	>1600	—	—	—	−794.96(c)	—



Calcium hydroxide	$Ca(OH)_2$	74.10	2.24			(−H_2O at 580°C)				−986.59(c)	—
Calcium oxide	CaO	56.08	3.32	2570	50	2850	—	—	—	−635.6(c)	—
Calcium phosphate	$Ca_3(PO_4)_2$	310.19	3.14	1670	—	—	—	—	—	−4138(c)	—
Calcium silicate	$CaSiO_3$	116.17	2.915	1530	48.62	—	—	—	—	−1584(c)	—
Calcium sulfate	$CaSO_4$	136.15	2.96	—	—	—	—	—	—	−1432.7(c) −1450.4(aq)	—
Calcium sulfate (gypsum)	$CaSO_4\cdot 2H_2O$	172.18	2.32		(−1.5 H_2O at 128°C)		—	—	—	−2021(c)	—
Carbon (graphite)	C	12.010	2.26	3600	46.0	4200	—	—	—	0(c)	−393.51(c)
Carbon dioxide	CO_2	44.01	—	−56.6 at 5.2 atm	8.33	(Sublimes at −78°C)		304.2	72.9	−412.9(l) −393.5(g)	— —
Carbon disulfide	CS_2	76.14	$1.261^{22°/20°}$	−112.1	4.39	46.25	26.8	552.0	78.0	+87.9(l) +115.3(g)	−1075.2(l) 1102.6(g)
Carbon monoxide	CO	28.01	—	−205.1	0.837	−191.5	6.042	133.0	34.5	−110.52(g)	−282.99(g)
Carbon tetrachloride	CCl	153.84	1.595	−22.9	2.51	76.7	30.0	556.4	45.0	−139.5(l) −106.7(g)	−352.2(l) −385.0(g)
Chlorine	Cl	70.91	—	−101.00	6.406	−34.06	20.4	417.0	76.1	0(g)	—
Chlorobenzene	$C\ H_5Cl$	112.56	1.107	−45	—	132.10	36.5	632.4	44.6	—	—
Chloroethane	H_5Cl	See ethyl chlo									

[a] Adapted in part from D. M. Himmelblau, *rinciples and Calculations in Chemical Engineering*, 3rd Edition, ©1974, Tables D.1 and F.1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

[b] Melting point at 1 atm.

[c] Heat of fusion at T_m and 1 atm.

[d] Boiling point at 1 atm.

[e] Heat of vaporization at T_b and 1 atm.

[f] Critical temperature.

[g] Critical pressure.

[h] Heat of formation at 25°C and 1 atm.

[i] Heat of combustion at 25°C and 1 atm. Standard states of products are $CO_2(g)$, $H_2O(l)$, $SO_2(g)$, $HCl(aq)$, and $N_2(g)$. To calculate $\Delta\hat{H}_c^\circ$ with $H_2O(g)$ as a product, add $44.01n_w$ to the tabulated value, where n_w = moles H_2O formed/mole fuel burned.

[j] To convert $\Delta\hat{H}$ to kcal/mol, divide given value by 4.184; to convert to Btu/lb-mole, multiply by 430.28.

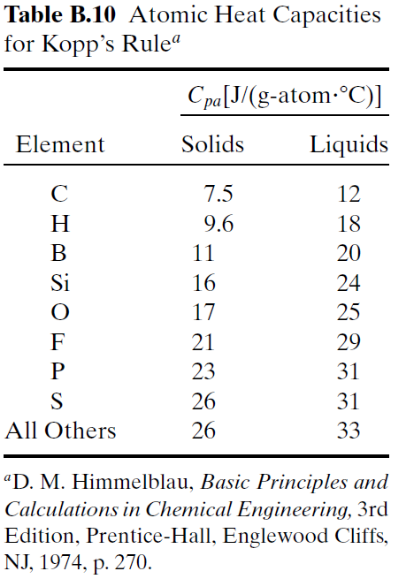


Table B.10 Atomic Heat Capacities for Kopp's Rule[a]

	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

[a] D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, Prentice-Hall, Englewood Cliffs, NJ, 1974, p. 270.

Kopp's Rule:

$$C_p = \sum_{k=element} \nu_k C_{p,k}$$

where ν_k = moles of element *k* in molecule

So for solid phenol, C_6H_5OH,

$\nu_C = 6$

$\nu_H = 6$

$\nu_O = 1$

$C_p = 6*7.5 + 6*9.6 + 17 = 119.6$ J/(mol·°C)

(Dippr = 129 J/(mol·°C) at 25°C)

Only use this out of desperation!

Other Estimation Formulas

- Trouton's rule (8.4-3)

$$\Delta H_v = f(T_b)$$

- Chen's equation (8.4-4)

$$\Delta H_v = f(T_b, T_c, P_c)$$

- Clapeyron equation (8.4-7)

$$\Delta H_v = f(P^*)$$

- Watson's correlation (8.4-8)

ΔH_v vs. T using T_c

Only use these equations out of desperation!

Simplifications

- Sometimes we get lazy and assume an average heat capacity for some temperature range

$$\hat{H}_2 - \hat{H}_1 = \overline{C_P}(T_2 - T_1)$$

- We will use this on exams!
  - I am not testing you on integration skills

Concepts

1. Enthalpy is a state function
2. Heat Capacities
3. Latent Heats (phase change)
4. Heat of Formation
5. Calculating ΔH as *f*(T,P)

Concept 4.
Heat of Formation

- Wanted: Common reference state for all species!
- Can use $\Delta\hat{H}_f^o$ as a reference at 25°C, 1 atm
- Good for reaction chemistry
- $\Delta\hat{H}_f^o$ = 0 for species whose natural state is 25°C, 1 atm
  - N_2, O_2, H_2, C(graphite)

$$\hat{H}_i = \Delta\hat{H}_{f,i}^o + \int_{25°\mathrm{C}}^{T_2} C_{P,i}\, dT$$

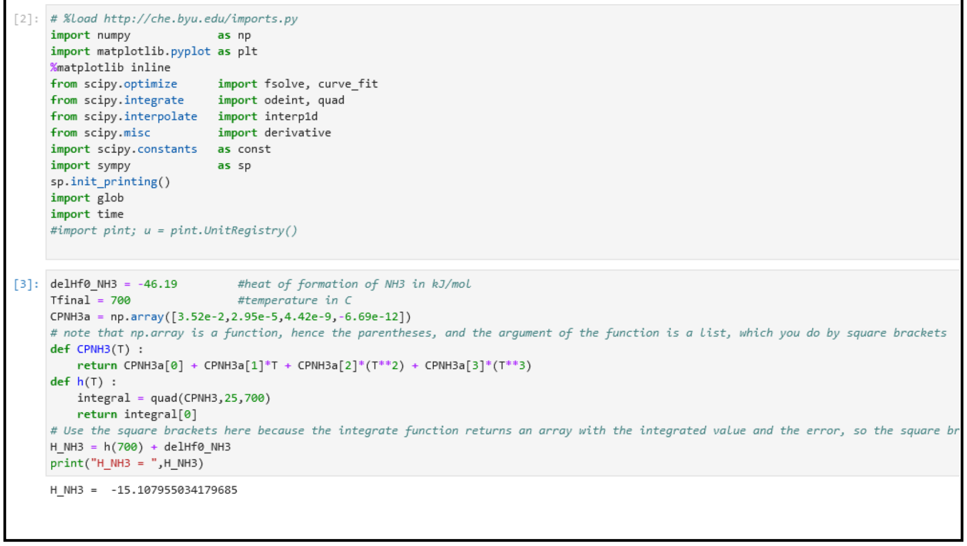
Tabulated in Table B.1

This equation is the "magic bullet" to solve all energy balances

$$\hat{H}_i = \Delta\hat{H}^o_{f,i} + \int_{25°C}^{T_2} C_{P,i}\, dT$$

Python Example

(Find $\hat{H}_{NH_3}$ at $700°C$)



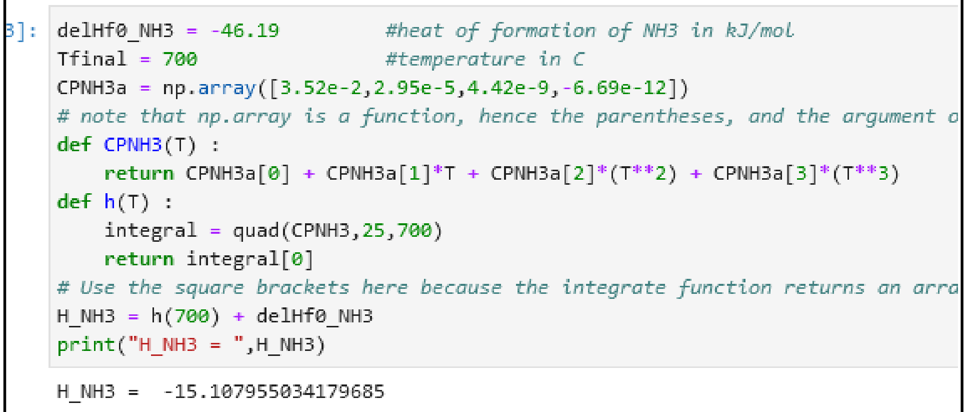
```
[2]: # %load http://che.byu.edu/imports.py
     import numpy                as np
     import matplotlib.pyplot as plt
     %matplotlib inline
     from scipy.optimize      import fsolve, curve_fit
     from scipy.integrate     import odeint, quad
     from scipy.interpolate   import interp1d
     from scipy.misc          import derivative
     import scipy.constants   as const
     import sympy             as sp
     sp.init_printing()
     import glob
     import time
     #import pint; u = pint.UnitRegistry()
```

```
[3]: delHf0_NH3 = -46.19          #heat of formation of NH3 in kJ/mol
     Tfinal = 700                 #temperature in C
     CPNH3a = np.array([3.52e-2,2.95e-5,4.42e-9,-6.69e-12])
     # note that np.array is a function, hence the parentheses, and the argument of the function is a list, which you do by square brackets
     def CPNH3(T) :
         return CPNH3a[0] + CPNH3a[1]*T + CPNH3a[2]*(T**2) + CPNH3a[3]*(T**3)
     def h(T) :
         integral = quad(CPNH3,25,700)
         return integral[0]
     # Use the square brackets here because the integrate function returns an array with the integrated value and the error, so the square br
     H_NH3 = h(700) + delHf0_NH3
     print("H_NH3 = ",H_NH3)
```

```
     H_NH3 =  -15.107955034179685
```

Python Example

(Find $\hat{H}_{NH_3}$ at 700°C)



```
delHf0_NH3 = -46.19          #heat of formation of NH3 in kJ/mol
Tfinal = 700                 #temperature in C
CPNH3a = np.array([3.52e-2,2.95e-5,4.42e-9,-6.69e-12])
# note that np.array is a function, hence the parentheses, and the argument o
def CPNH3(T) :
    return CPNH3a[0] + CPNH3a[1]*T + CPNH3a[2]*(T**2) + CPNH3a[3]*(T**3)
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```

```
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```

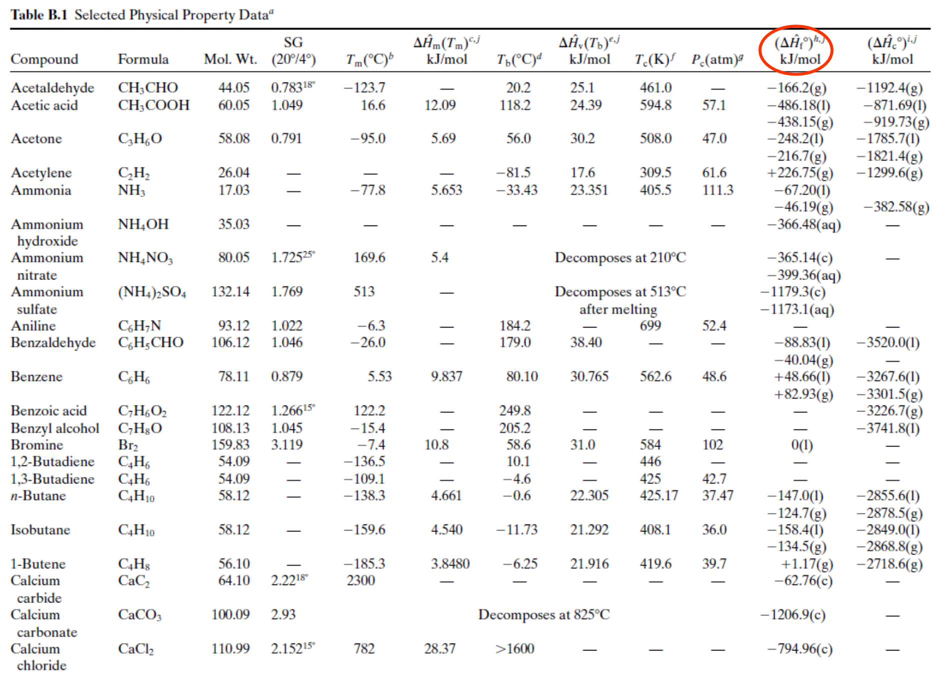


Table B.1 Selected Physical Property Data[a]

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m(°C)[b]	$\Delta\hat{H}_m(T_m)^{c,j}$ kJ/mol	T_b(°C)[d]	$\Delta\hat{H}_v(T_b)^{e,j}$ kJ/mol	T_c(K)[f]	P_c(atm)[g]	$(\Delta\hat{H}_f^\circ)^{h,j}$ kJ/mol	$(\Delta\hat{H}_c^\circ)^{i,j}$ kJ/mol
Acetaldehyde	CH_3CHO	44.05	$0.783^{18°}$	−123.7	—	20.2	25.1	461.0	—	−166.2(g)	−1192.4(g)
Acetic acid	CH_3COOH	60.05	1.049	16.6	12.09	118.2	24.39	594.8	57.1	−486.18(l) −438.15(g)	−871.69(l) −919.73(g)
Acetone	C_3H_6O	58.08	0.791	−95.0	5.69	56.0	30.2	508.0	47.0	−248.2(l) −216.7(g)	−1785.7(l) −1821.4(g)
Acetylene	C_2H_2	26.04	—	—	—	−81.5	17.6	309.5	61.6	+226.75(g)	−1299.6(g)
Ammonia	NH_3	17.03	—	−77.8	5.653	−33.43	23.351	405.5	111.3	−67.20(l) −46.19(g)	−382.58(g)
Ammonium hydroxide	NH_4OH	35.03	—	—	—	—	—	—	—	−366.48(aq)	—
Ammonium nitrate	NH_4NO_3	80.05	$1.725^{25°}$	169.6	5.4	Decomposes at 210°C				−365.14(c) −399.36(aq)	—
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	1.769	513	—	Decomposes at 513°C after melting				−1179.3(c) −1173.1(aq)	
Aniline	C_6H_7N	93.12	1.022	−6.3	—	184.2	—	699	52.4	—	—
Benzaldehyde	C_6H_5CHO	106.12	1.046	−26.0	—	179.0	38.40	—	—	−88.83(l) −40.04(g)	−3520.0(l) —
Benzene	C_6H_6	78.11	0.879	5.53	9.837	80.10	30.765	562.6	48.6	+48.66(l) +82.93(g)	−3267.6(l) −3301.5(g)
Benzoic acid	$C_7H_6O_2$	122.12	$1.266^{15°}$	122.2	—	249.8	—	—	—	—	−3226.7(g)
Benzyl alcohol	C_7H_8O	108.13	1.045	−15.4	—	205.2	—	—	—	—	−3741.8(l)
Bromine	Br_2	159.83	3.119	−7.4	10.8	58.6	31.0	584	102	0(l)	—
1,2-Butadiene	C_4H_6	54.09	—	−136.5	—	10.1	—	446	—	—	—
1,3-Butadiene	C_4H_6	54.09	—	−109.1	—	−4.6	—	425	42.7	—	—
n-Butane	C_4H_{10}	58.12	—	−138.3	4.661	−0.6	22.305	425.17	37.47	−147.0(l) −124.7(g)	−2855.6(l) −2878.5(g)
Isobutane	C_4H_{10}	58.12	—	−159.6	4.540	−11.73	21.292	408.1	36.0	−158.4(l) −134.5(g)	−2849.0(l) −2868.8(g)
1-Butene	C_4H_8	56.10	—	−185.3	3.8480	−6.25	21.916	419.6	39.7	+1.17(g)	−2718.6(g)
Calcium carbide	CaC_2	64.10	$2.22^{18°}$	2300	—	—	—	—	—	−62.76(c)	—
Calcium carbonate	$CaCO_3$	100.09	2.93	Decomposes at 825°C						−1206.9(c)	—
Calcium chloride	$CaCl_2$	110.99	$2.152^{15°}$	782	28.37	>1600	—	—	—	−794.96(c)	—

Balances

$$\Delta H_{sys} = H_{out} - H_{in}$$

$$\Delta H_{sys} = \left(\sum n_i \hat{H}_i\right)_{out} - \left(\sum n_i \hat{H}_i\right)_{in}$$

$$\hat{H}_i = \Delta\hat{H}^o_{f,i} + \int_{25°\mathrm{C}}^{T_2} C_{P,i}\, dT$$

$$\sum n_i \hat{H}_i = \sum n_i \Delta\hat{H}^o_{f,i} + \left(\sum n_i \left[a_i(T-298)\right]\right) + \left(\sum n_i \left[b_i \frac{T^2-298^2}{2}\right]\right) + \left(\sum n_i \left[c_i\right]\frac{T^3-298^3}{3}\right) + \cdots$$

$$\sum n_i \hat{H}_i = \sum n_i \Delta\hat{H}^o_{f,i} + \left(\sum n_i a_i\right)(T-298) + \left(\sum n_i b_i\right)\frac{T^2-298^2}{2} + \left(\sum n_i c_i\right)\frac{T^3-298^3}{3} + \cdots$$

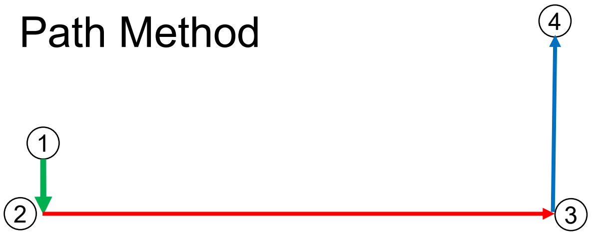
where a_i, b_i, and c_i are the heat capacity coefficients for species i

Note that for a chemical reaction, the number of moles of each species (n_i) changes

---

Two Methods to Get ΔH

1. Path Method



$$H_4 - H_1 = (\boldsymbol{H_2 - H_1}) + (\boldsymbol{H_3 - H_2}) + (\boldsymbol{H_4 - H_3})$$

2. ΔH_f^0 method

$$\hat{H}_i = \Delta\hat{H}^o_{f,i} + \int_{25°\mathrm{C}}^{T_2} C_{P,i}\, dT$$

So compute H_4 and H_1 and subtract

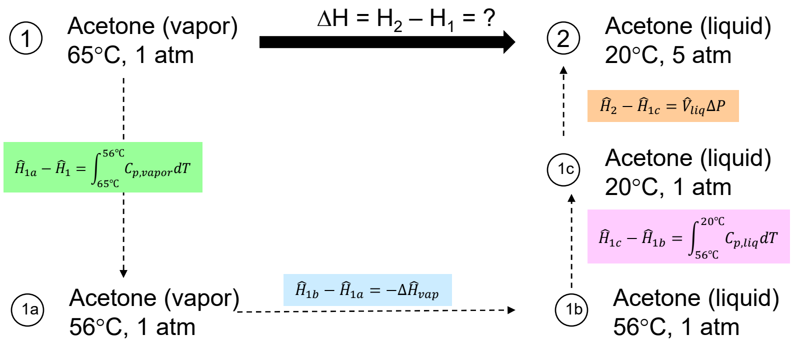
Example

Calculate the enthalpy change for acetone going from a vapor at 65°C and 1 atm to a liquid at 20 °C and 5 atm

A. Path method using ΔH_{vap} at 1 atm and $T_{boiling}$

B. Heat of formation method

Example: Find ΔH for acetone vapor at 65°C forming a liquid at 20 °C and 5 atm (Path method)



① Acetone (vapor)
65°C, 1 atm

$\Delta H = H_2 - H_1 = ?$

② Acetone (liquid)
20°C, 5 atm

$\hat{H}_2 - \hat{H}_{1c} = \hat{V}_{liq}\Delta P$

$\hat{H}_{1a} - \hat{H}_1 = \int_{65°C}^{56°C} C_{p,vapor}dT$

1c Acetone (liquid)
20°C, 1 atm

$\hat{H}_{1c} - \hat{H}_{1b} = \int_{56°C}^{20°C} C_{p,liq}dT$

1a Acetone (vapor)
56°C, 1 atm

$\hat{H}_{1b} - \hat{H}_{1a} = -\Delta\hat{H}_{vap}$

1b Acetone (liquid)
56°C, 1 atm

$$\hat{H}_2 - \hat{H}_1 = (\hat{H}_{1a} - \hat{H}_1) + (\hat{H}_{1b} - \hat{H}_{1a}) + (\hat{H}_{1ac} - \hat{H}_{1b}) + (\hat{H}_2 - \hat{H}_{1c})$$

$$\hat{H}_2 - \hat{H}_1 = \int_{65°C}^{56°C} C_{p,vapor}dT + (-\Delta\hat{H}_{vap,56°C}) + \int_{56°C}^{20°C} C_{p,liq}dT + \hat{V}_{liq}\Delta P$$

Example: Find ΔH for acetone vapor at 65°C forming a liquid at 20 °C and 5 atm (ΔH_f^o method)

① Acetone (vapor)
65°C, 1 atm

$\Delta H = H_2 - H_1 = ?$ →

② Acetone (liquid)
20°C, 5 atm

$$\hat{H}_1 = \Delta H^{\circ}_{f,vapor} + \int_{25℃}^{65℃} C_{p,vapor}\,dT$$

$$\hat{H}_2 = \Delta H^{\circ}_{f,liq} + \int_{25℃}^{20℃} C_{p,liq}\,dT + \hat{V}_{liq}\Delta P$$

$$\hat{H}_2 - \hat{H}_1 = \left(\Delta H^{\circ}_{f,liq} + \int_{25℃}^{20℃} C_{p,liq}\,dT + \hat{V}_{liq}\Delta P\right) - \left(\Delta H^{\circ}_{f,vapor} + \int_{25℃}^{65℃} C_{p,vapor}\,dT\right)$$

$$\hat{H}_2 - \hat{H}_1 = \underbrace{\Delta H^{\circ}_{f,liq} - \Delta H^{\circ}_{f,vapor}}_{-\Delta H_{vaporization}\ at\ 25℃} + \int_{25℃}^{20℃} C_{p,liq}\,dT + \hat{V}_{liq}\Delta P - \int_{25℃}^{65℃} C_{p,vapor}\,dT$$

See Excel Sheet

Path vs ΔH_f^o method

Bottom Line

You Should Know Both Methods to Get ΔH

1. Path Method
2. ΔH_f^o method

Remember that ΔH is just part of energy balance

$$\Delta\dot{H} + \Delta\dot{E}_K + \Delta\dot{E}_P = \dot{Q} + \dot{W}_s$$

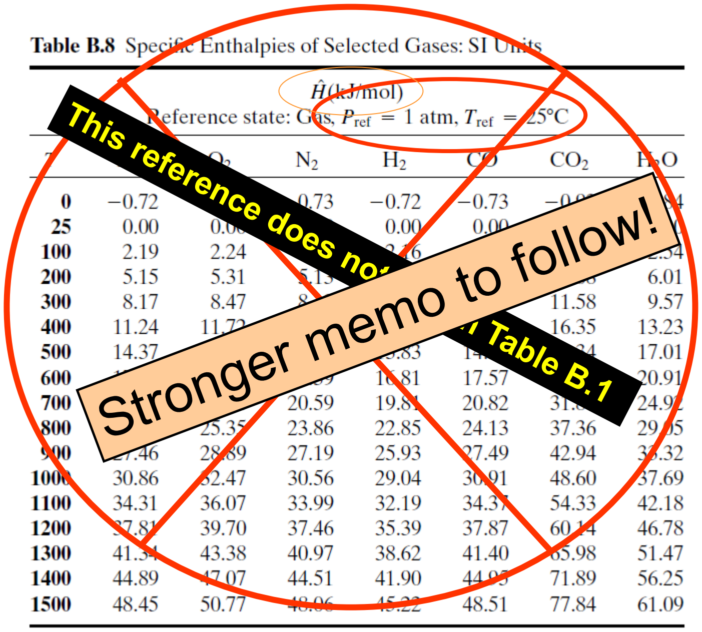


Table B.8 Specific Enthalpies of Selected Gases: SI Units

$\hat{H}$(kJ/mol)

Reference state: Gas, P_{ref} = 1 atm, T_{ref} = 25°C

T	[illegible]	O_2	N_2	H_2	CO	CO_2	H_2O
0	−0.72	[illegible]	[illegible]	−0.72	−0.73	[illegible]	[illegible]
25	0.00	[illegible]	[illegible]	0.00	0.00	[illegible]	[illegible]
100	2.19	2.24	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
200	5.15	5.31	[illegible]	[illegible]	[illegible]	[illegible]	6.01
300	8.17	8.47	[illegible]	[illegible]	[illegible]	11.58	9.57
400	11.24	11.72	[illegible]	[illegible]	[illegible]	16.35	13.23
500	14.37	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	17.01
600	[illegible]	[illegible]	[illegible]	16.81	17.57	[illegible]	20.91
700	[illegible]	[illegible]	20.59	19.81	20.82	[illegible]	24.92
800	[illegible]	25.35	23.86	22.85	24.13	37.36	29.05
900	27.46	28.89	27.19	25.93	27.49	42.94	33.32
1000	30.86	32.47	30.56	29.04	30.91	48.60	37.69
1100	34.31	36.07	33.99	32.19	34.37	54.33	42.18
1200	37.81	39.70	37.46	35.39	37.87	60.14	46.78
1300	41.34	43.38	40.97	38.62	41.40	65.98	51.47
1400	44.89	47.07	44.51	41.90	44.95	71.89	56.25
1500	48.45	50.77	48.06	45.22	48.51	77.84	61.09

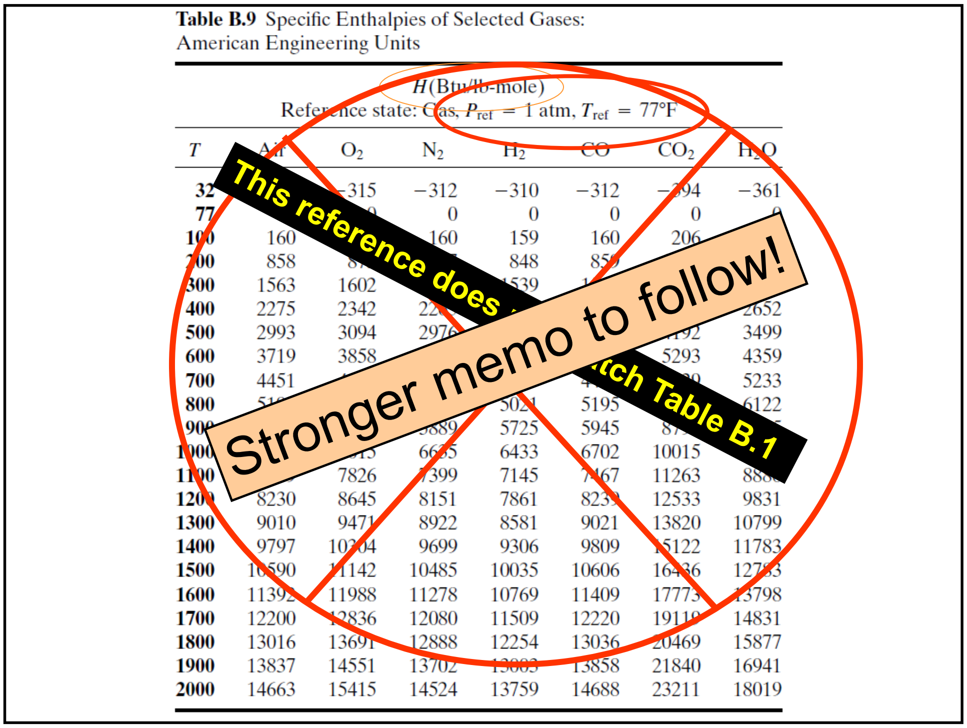


Table B.9 Specific Enthalpies of Selected Gases: American Engineering Units

$\hat{H}$(Btu/lb-mole)
Reference state: Gas, $P_{\text{ref}} = 1$ atm, $T_{\text{ref}} = 77°\text{F}$

T	Air	O_2	N_2	H_2	CO	CO_2	H_2O
32	[illegible]	−315	−312	−310	−312	−394	−361
77	[illegible]	0	0	0	0	0	0
100	160	[illegible]	160	159	160	206	[illegible]
200	858	[illegible]	[illegible]	848	859	[illegible]	[illegible]
300	1563	1602	[illegible]	1539	[illegible]	[illegible]	[illegible]
400	2275	2342	[illegible]	[illegible]	[illegible]	[illegible]	2652
500	2993	3094	2976	[illegible]	[illegible]	[illegible]	3499
600	3719	3858	[illegible]	[illegible]	[illegible]	5293	4359
700	4451	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	5233
800	[illegible]	[illegible]	[illegible]	5021	5195	[illegible]	6122
900	[illegible]	[illegible]	[illegible]	5725	5945	[illegible]	[illegible]
1000	[illegible]	[illegible]	[illegible]	6433	6702	10015	[illegible]
1100	[illegible]	7826	7399	7145	7467	11263	[illegible]
1200	8230	8645	8151	7861	8239	12533	9831
1300	9010	9471	8922	8581	9021	13820	10799
1400	9797	10304	9699	9306	9809	15122	11783
1500	10590	11142	10485	10035	10606	16436	12783
1600	11392	11988	11278	10769	11409	17773	13798
1700	12200	12836	12080	11509	12220	19119	14831
1800	13016	13691	12888	12254	13036	20469	15877
1900	13837	14551	13702	13003	13858	21840	16941
2000	14663	15415	14524	13759	14688	23211	18019

This reference does [illegible]tch Table B.1

Stronger memo to follow!

Taboo Equations

3rd Edition

- Page 451: 9.5-1a and 9.5-1b
- 1st Eqn. on page 457
- Page 463: last equation (under section 5)

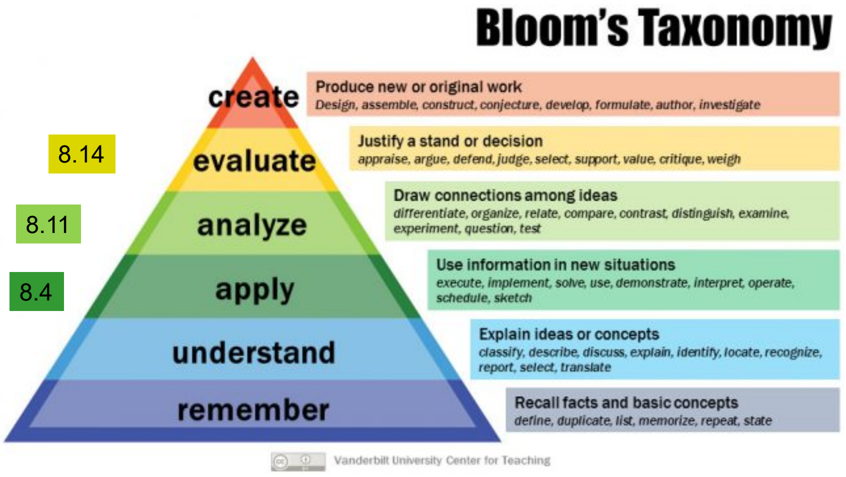
4th Edition

- Page 506: 9.5-1a and 9.5-1b
- 1st Eqn. on page 511
- Page 519: last equation (under section 5)

Problem Solving (pp. 361-362)

1. Solve material balances (mass or moles)
2. Write energy balance (drop appropriate terms)
3. Choose reference state(s)
4. Table of n_i & H_i in and out (or m_i, U_i, etc.)
5. Find ΔH_{sys} or ΔU_{sys}
6. Find W, W_s, ΔE_k, ΔE_p as needed
7. Solve energy balance

Homework Problems



Bloom's Taxonomy

8.14

8.11

8.4

create — Produce new or original work
Design, assemble, construct, conjecture, develop, formulate, author, investigate

evaluate — Justify a stand or decision
appraise, argue, defend, judge, select, support, value, critique, weigh

analyze — Draw connections among ideas
differentiate, organize, relate, compare, contrast, distinguish, examine, experiment, question, test

apply — Use information in new situations
execute, implement, solve, use, demonstrate, interpret, operate, schedule, sketch

understand — Explain ideas or concepts
classify, describe, discuss, explain, identify, locate, recognize, report, select, translate

remember — Recall facts and basic concepts
define, duplicate, list, memorize, repeat, state

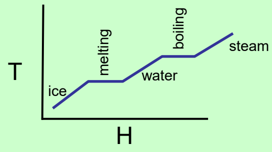
Vanderbilt University Center for Teaching

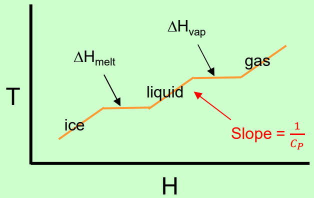
https://cft.vanderbilt.edu/guides-sub-pages/blooms-taxonomy/

QUIZ

1. What is meant by the statement that “enthalpy is a state function?”
2. What is a heat capacity?
3. For water, draw a graph with temperature on the *y* axis and enthalpy on the *x* axis, starting from ice and proceeding to steam, labeling the different portions of the line.
4. How do you use the heat of formation to calculate enthalpy? (eqn. needed)

1. What is meant by the statement that “enthalpy is a state function?”
   - H is not dependent on T & P path
2. What is a heat capacity?
   - Change in enthalpy with temperature
3. For water, draw a graph with temperature on the *y* axis and enthalpy on the *x* axis, starting from ice and proceeding to steam, labeling the different portions of the line.





4. How do you use the heat of formation to calculate enthalpy?

$$H(at\ T_2) = \Delta H_f^0 + \int_{T_1=25°C}^{T_2} C_p dT$$