

Class 28

Enthalpies, Heat Capacities, Oh My!

Table B.1 Selected Physical Property Data*

| Compound | Formula | Mol. Wt. (g/mol) | T_m (°C) | T_b (°C) | T_c (°C) | T_f (K) | P_f (atm) | ΔH_f (kJ/mol) | ΔH_v (kJ/mol) | | |
|--------------------|---|------------------|---------------------|------------|------------|-----------|-------------|-----------------------|-----------------------|------------|------------|
| Acetaldehyde | CH ₃ CHO | 44.05 | 0.763 ¹⁰ | -123.7 | — | 25.1 | 81.0 | -166.2(3) | -1192.4(3) | | |
| Acetic acid | CH ₃ COOH | 60.05 | 1.649 | 16.6 | 12.00 | 118.2 | 24.39 | 948.8 | 57.1 | -486.1(3) | -871.6(3) |
| Acrylonitrile | C ₃ H _{3.5} N | 53.05 | — | -95.0 | 5.69 | 56.0 | 30.2 | 508.0 | 47.0 | -438.15(3) | -919.73(3) |
| Ammonia | NH ₃ | 17.03 | — | -77.8 | 5.653 | -33.43 | 24.351 | 468.5 | 111.3 | -248.2(3) | -1785.7(3) |
| Ammonium hydroxide | NH ₄ OH | 35.05 | — | — | — | — | — | — | — | -46.19(3) | -382.58(3) |
| Ammonium nitrate | NH ₄ NO ₃ | 80.05 | 1.725 ¹⁰ | 169.6 | 5.4 | — | — | — | — | -365.14(3) | — |
| Ammonium sulfate | (NH ₄) ₂ SO ₄ | 132.14 | 1.769 | 513 | — | — | — | — | — | -999.36(3) | — |
| Aniline | C ₆ H ₅ N | 93.12 | 1.022 | -6.3 | — | 184.2 | — | — | — | -1179.3(3) | — |
| Benzene | C ₆ H ₆ | 78.11 | 0.879 | 5.53 | 9.837 | 40.10 | 30.765 | 562.6 | 48.6 | -85.83(3) | -3203.0(3) |
| Benzonic acid | C ₇ H ₆ O ₂ | 122.12 | 1.260 ¹⁰ | 122.2 | — | 249.8 | — | — | — | -40.04(3) | — |
| Bromine | Br ₂ | 159.83 | 3.119 | -7.4 | 10.8 | 58.6 | 31.0 | 584 | 102 | -48.94(3) | -3741.8(3) |
| 1,2-Butanediol | C ₄ H ₁₀ O ₂ | 54.09 | — | -136.5 | — | 10.1 | — | — | — | -326.7(3) | — |
| n-Butane | C ₄ H ₁₀ | 58.12 | — | -138.3 | 4.661 | -0.6 | 22.305 | 425.17 | 37.47 | -147.0(3) | -2855.0(3) |
| Isobutane | C ₄ H ₁₀ | 58.12 | — | -159.6 | 4.540 | -11.73 | 21.292 | 408.1 | 36.0 | -124.7(3) | -2878.5(3) |
| n-Butane carbonate | C ₄ H ₈ O ₃ | 56.10 | — | -105.3 | 3.8460 | -6.25 | 21.916 | 419.6 | 39.7 | -134.5(3) | -2868.3(3) |
| Calcium carbonate | CaCO ₃ | 100.09 | 2.90 | — | — | — | — | — | — | -1206.9(3) | — |
| Calcium chloride | CaCl ₂ | 110.99 | 2.152 ¹⁰ | 782 | 28.37 | >1600 | — | — | — | -794.96(3) | — |

| Compound | Formula | Mol. Wt. (g/mol) | T_m (°C) | T_b (°C) | T_c (°C) | T_f (K) | P_f (atm) | ΔH_f (kJ/mol) | ΔH_v (kJ/mol) | | |
|---------------------------|---|------------------|---------------------|------------|------------|---------------------|-------------|-----------------------|-----------------------|------------|------------|
| Calcium hydroxide | Ca(OH) ₂ | 74.10 | 2.24 | — | — | — | — | -986.59(3) | — | | |
| Calcium oxide | CaO | 56.08 | 3.32 | 2570 | 50 | 2850 | — | -635.6(3) | — | | |
| Calcium phosphate | Ca ₃ (PO ₄) ₂ | 310.19 | 3.14 | 1620 | — | — | — | -4138(3) | — | | |
| Calcium silicate | CaSiO ₃ | 116.17 | 2.915 | 1530 | 48.62 | — | — | -1584(3) | — | | |
| Calcium sulfate | CaSO ₄ | 136.15 | 2.96 | — | — | — | — | -1432.7(3) | — | | |
| Calcium sulfate dihydrate | CaSO ₄ ·2H ₂ O | 172.18 | 2.32 | — | — | — | — | -1450.4(3) | — | | |
| Carbon (graphite) | C | 12.010 | 2.26 | 3600 | 46.0 | 4300 | — | 0(3) | -390.51(3) | | |
| Carbon dioxide | CO ₂ | 44.01 | — | -56.6 | 8.33 | (Sublimes at -78°C) | 304.2 | 72.9 | — | -42.83(3) | — |
| Carbon disulfide | CS ₂ | 76.14 | 1.261 ¹⁰ | -112.1 | 4.39 | 46.25 | 26.8 | 552.0 | 78.0 | -87.9(3) | -1075.2(3) |
| Carbon monoxide | CO | 28.01 | — | -208.1 | 0.837 | -191.5 | 6.042 | 133.0 | 34.5 | -110.52(3) | -102.1(3) |
| Carbon monoxide monoxide | C ₂ O | 153.84 | 1.998 | -72.9 | 2.51 | 26.7 | 36.0 | 556.4 | 45.0 | -139.5(3) | -352.0(3) |
| Carbon tetrachloride | CCl ₄ | 153.84 | — | -101.0 | 6.406 | -34.06 | 20.4 | 417.0 | 78.1 | 0(3) | — |
| Chloroacetylene | C ₂ HCl | 112.56 | 1.107 | -65 | — | 132.10 | 36.5 | 602.4 | 41.6 | — | — |

*Adapted in part from D. M. Himmelblau, *Basic Principles and Calculations in Chemical Engineering*, 3rd Edition, ©1974, Tables D1 and F1. Adapted by permission of Prentice-Hall, Inc., Englewood Cliffs, NJ.

†Melting point at 1 atm.
‡Heat of fusion at T_m and 1 atm.
§Boiling point at 1 atm.
¶Heat of vaporization at T_b and 1 atm.
**Critical pressure.
***Heat of formation at 25°C and 1 atm.
****Heat of combustion at 25°C and 1 atm. Standard states of products are CO₂(g), H₂O(l), SO₂(g), HCl(aq), and N₂(g). To calculate ΔH_f° with H₂O(g) as a product, add 44.01 kJ to the tabulated value, where ΔH_c° = moles H₂O formed/mole fuel burned.
*****To convert ΔH_f° to kcal/mol, divide given value by 4.184, to convert to Btu/mol, multiply by 430.25.

Table B.2 Heat Capacities*

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 (kJ/mol·°C) = $0.07196 + (20.10 \times 10^{-5})T + (12.78 \times 10^{-7})T^2 + (34.76 \times 10^{-10})T^3$, 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. (g/mol) | State | Form | a (kJ/mol·°C) | b (kJ/mol·°C ²) | c (kJ/mol·°C ³) | d (kJ/mol·°C ⁴) | Range (Temp. (°C)) |
|----------------------|---|------------------|-------|------|-----------------|-------------------------------|-------------------------------|-------------------------------|--------------------|
| Acetone | CH ₃ COCH ₃ | 58.08 | l | 1 | 123.0 | 18.6 | -12.78 | 34.76 | 30-90 |
| Acetylene | C ₂ H ₂ | 26.04 | g | 1 | 42.43 | 6.053 | -5.033 | 18.20 | 0-2000 |
| Air | | 29.0 | g | 1 | 28.94 | 0.4147 | 0.3191 | -1.965 | 0-2000 |
| Ammonia | NH ₃ | 17.03 | g | 1 | 28.09 | 0.1965 | 0.4799 | -1.985 | 273-1000 |
| Ammonium sulfate | (NH ₄) ₂ SO ₄ | 132.15 | s | 2 | 35.15 | 2.854 | 0.4423 | -6.680 | 0-2000 |
| Benzene | C ₆ H ₆ | 78.11 | l | 1 | 126.5 | 23.4 | -25.20 | 77.57 | 0-2000 |
| Isobutane | C ₄ H ₁₀ | 58.12 | g | 1 | 89.46 | 30.13 | -18.91 | 49.87 | 0-2000 |
| n-Butane | C ₄ H ₁₀ | 58.12 | g | 1 | 92.30 | 27.88 | -15.47 | 34.88 | 0-2000 |
| Isobutane | C ₄ H ₁₀ | 58.10 | g | 1 | 82.88 | 28.64 | -17.27 | 50.50 | 0-2000 |
| Calcium carbonate | CaCO ₃ | 64.10 | s | 2 | 66.62 | 1.19 | -8.66 × 10 ⁻⁶ | — | 298-275 |
| Calcium hydroxide | Ca(OH) ₂ | 74.10 | s | 2 | 82.34 | 4.975 | -12.87 × 10 ⁻⁶ | — | 273-1033 |
| Calcium oxide | CaO | 56.08 | s | 2 | 89.5 | 2.03 | -4.57 × 10 ⁻⁶ | — | 273-275 |
| Carbon | C | 12.01 | s | 2 | 11.8 | 1.095 | -4.801 × 10 ⁻⁶ | — | 273-1174 |
| Carbon dioxide | CO ₂ | 44.01 | g | 1 | 30.11 | 4.233 | -2.887 | 7.464 | 0-1500 |
| Carbon monoxide | CO | 28.01 | g | 1 | 23.95 | 0.4110 | 0.3548 | -2.220 | 0-1500 |
| Carbon tetrachloride | CCl ₄ | 153.84 | l | 1 | 93.39 | 12.88 | — | — | 273-343 |
| Chloroacetylene | C ₂ HCl | 70.91 | g | 1 | 38.60 | 1.367 | -1.607 | 6.473 | 0-1263 |
| Copper | Cu | 63.54 | s | 2 | 22.76 | 0.6117 | — | — | 273-1357 |

*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.8, use the multiplier at the top of the column
- Example: Acetone
 - a = 123
 - multiplier = 10³
 - Therefore, a = 123 × 10⁻³ kJ/(gmol·K)

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

Reference state: Gas, $P_{ref} = 1 \text{ atm}$, $T_{ref} = 25^\circ\text{C}$

| θ (K) | O ₂ | N ₂ | H ₂ | CO | CO ₂ | H ₂ O |
|--------------|----------------|----------------|----------------|-------|-----------------|------------------|
| 0 | 0.000 | -0.73 | -0.72 | -0.73 | -0.92 | -84 |
| 25 | 0.000 | 0.00 | 0.00 | 0.00 | 0.00 | 0 |
| 100 | 2.19 | 1.99 | 2.16 | 2.19 | 2.19 | 2.19 |
| 200 | 5.15 | 5.31 | 5.09 | 5.15 | 5.15 | 5.15 |
| 300 | 8.17 | 8.47 | 8.11 | 8.17 | 8.17 | 8.17 |
| 400 | 11.24 | 11.72 | 11.24 | 11.24 | 11.24 | 11.24 |
| 500 | 14.37 | 15.03 | 14.37 | 14.37 | 14.37 | 14.37 |
| 600 | 17.55 | 18.03 | 17.55 | 17.55 | 17.55 | 17.55 |
| 700 | 20.77 | 20.81 | 20.77 | 20.77 | 20.77 | 20.77 |
| 800 | 24.03 | 23.56 | 24.03 | 24.03 | 24.03 | 24.03 |
| 900 | 27.33 | 27.19 | 27.33 | 27.33 | 27.33 | 27.33 |
| 1000 | 30.67 | 30.56 | 30.67 | 30.67 | 30.67 | 30.67 |
| 1100 | 34.05 | 33.99 | 34.05 | 34.05 | 34.05 | 34.05 |
| 1200 | 37.47 | 37.46 | 37.47 | 37.47 | 37.47 | 37.47 |
| 1300 | 40.93 | 40.97 | 40.93 | 40.93 | 40.93 | 40.93 |
| 1400 | 44.43 | 44.51 | 44.43 | 44.43 | 44.43 | 44.43 |
| 1500 | 47.97 | 48.06 | 47.97 | 47.97 | 47.97 | 47.97 |

This reference does not follow!
Stronger memo to follow!

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

Reference state: $O_2, F_{ref} = 1 \text{ atm}, T_{ref} = 77^\circ\text{F}$

B (Btu/(lb-mole))

| T | O ₂ | N ₂ | H ₂ | CO | CO ₂ | H ₂ O |
|------|----------------|----------------|----------------|-------|-----------------|------------------|
| 77 | 0 | -312 | -310 | -312 | 394 | -361 |
| 100 | 160 | 160 | 159 | 160 | 206 | 160 |
| 200 | 858 | 875 | 875 | 875 | 1059 | 858 |
| 300 | 1563 | 1602 | 1599 | 1602 | 1882 | 1563 |
| 400 | 2275 | 2342 | 2265 | 2342 | 2659 | 2275 |
| 500 | 2993 | 3094 | 2970 | 3094 | 3499 | 2993 |
| 600 | 3719 | 3858 | 3690 | 3858 | 4359 | 3719 |
| 700 | 4451 | 4635 | 4422 | 4635 | 5219 | 4451 |
| 800 | 5189 | 5397 | 5222 | 5397 | 6079 | 5189 |
| 900 | 5933 | 6175 | 6045 | 6175 | 6939 | 5933 |
| 1000 | 6683 | 6965 | 6802 | 6965 | 7802 | 6683 |
| 1100 | 7439 | 7775 | 7575 | 7775 | 8668 | 7439 |
| 1200 | 8201 | 8605 | 8365 | 8605 | 9538 | 8201 |
| 1300 | 8969 | 9455 | 9185 | 9455 | 10412 | 8969 |
| 1400 | 9743 | 10325 | 10015 | 10325 | 11292 | 9743 |
| 1500 | 10523 | 11215 | 10865 | 11215 | 12178 | 10523 |
| 1600 | 11309 | 12125 | 11785 | 12125 | 13072 | 11309 |
| 1700 | 12101 | 13055 | 12725 | 13055 | 13972 | 12101 |
| 1800 | 12901 | 14005 | 13685 | 14005 | 14878 | 12901 |
| 1900 | 13709 | 14975 | 14665 | 14975 | 15792 | 13709 |
| 2000 | 14525 | 15965 | 15665 | 15965 | 16712 | 14525 |

Stronger memo to follow!

This reference does not follow!

Table B.1

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

| Element | C_p [J/(g-atom·°C)] | |
|------------|-----------------------|---------|
| | 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 |

Kopp's Rule:

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

where v_k = moles of element k in molecule

So for solid C_6H_5OH ,

$$C_p = 6(7.5) + 6(9.6) + 17 = 119.6 \text{ J/(mol·°C)}$$

(Dippr = 129 J/(mol·°C) at 25°C)

Only use this out of desperation!

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

- ### Other Estimation Formulas
- Trouton's rule (for ΔH_v) (8.4-3)
 - Chen's equation (for ΔH_v) (8.4-4)
 - Clapeyron equation (ΔH_v vs. T) (8.4-7)
 - Watson's correlation (ΔH_v vs. T using T_c) (8.4-8)

- ### 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

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?