

**First Law of Thermodynamics**

**Constants and Conversion Factors**

1 Pa	1 N m <sup>-2</sup> , 1 kg m <sup>-1</sup> s <sup>-2</sup>
1 bar	10 <sup>5</sup> Pa
1 atm	101.325 kPa
Torr	101325/760 = 133.32 Pa
1 mmHg	133.32 Pa
1 psi	6.894 kPa
1 liter	1000.028 cm <sup>3</sup>
1 atm	1.01325 x 10 <sup>6</sup> dynes cm <sup>-2</sup>
1 cal	4.1833 joules
1 volt-coulombs	1 joules
	0.01 liter-atm
	10 cc-atm
1 liter-atm	1.0133 x 10 <sup>9</sup> ergs
	1.0133 x 10 <sup>9</sup> joules
	24.218 cal
1 cc-atm	0.024212 cal
Molar volume of ideal gas at 0 °C and 1 atm	22.4140 liter mole <sup>-1</sup>
Ice Point	273.16 K
Molar gas constant (R)	8.3144 joules K <sup>-1</sup> mole <sup>-1</sup>
	1.9872 cal K <sup>-1</sup> mole <sup>-1</sup>
	0.082054 liter-atm. K <sup>-1</sup> mole <sup>-1</sup>
	82.057 cc.-atm. K <sup>-1</sup> mole <sup>-1</sup>
Avogadro number (N)	6.0228 x 10 <sup>23</sup> mole <sup>-1</sup>
Boltzmann constant (k = R/N)	1.3805 x 10 <sup>-16</sup> erg K <sup>-1</sup>
Planck constant (h)	6.6242 x 10 <sup>-27</sup> erg sec
6.6242 x 10 <sup>-34</sup> joules sec	
Velocity of light (c)	2.99776 x 10 <sup>10</sup> cm sec <sup>-1</sup>
Faraday (F)	96,500 coulombs mol <sup>-1</sup>
	23,070 cal. volt <sup>-1</sup> mol <sup>-1</sup>

*Problems*

1. A substance expands by 1 liter against a constant pressure of 1 atm. Calculate the work done in (a) liter-atm., (b) newton-meter, (c) ergs, (d) joules, (e) calories.
2. A quantity of 50 coulombs of electricity flows through a conductor under the influence of a potential of 2 volts. Calculate the energy expenditure in (a) joules, (b) ergs, (c) calories.
3. The specific volume of liquid acetic acid exceeds that of the solid at the melting point by  $0.1595 \text{ cc g}^{-1}$  at 1 atm pressure. Determine the work of expansion, in calories, and in joules accompanying the fusion of 2 mole of acetic acid at atmospheric pressure.
4. Calculate the work done against a constant pressure of 700.0 mm when 1 mole of water evaporates completely at  $100^\circ\text{C}$ ; the specific volume of water is approximately  $1 \text{ cc g}^{-1}$  and that of the vapor is  $1720 \text{ cc g}^{-1}$ . Express the results in (i) ergs, (ii) liter-atm., (iii) joules, (iv) N-m, (v) cal.
5. The density of mercury at  $0^\circ\text{C}$  and 1 atm pressure is  $13.595 \text{ g cc}^{-1}$ . Determine the work of expansion in ergs when the temperature of 100 g of mercury is raised from  $0^\circ\text{C}$  to  $100^\circ\text{C}$  at 1 atm pressure. Given that the mean specific heat in this range is  $0.0330 \text{ cal deg}^{-1} \text{ g}^{-1}$ , what proportion of the total amount of heat supplied to the mercury is the work of expansion?
6. The faraday is usually given as 96,488 coulombs per mol; show that it is also equal to  $23,070 \text{ cal volt}^{-1} \text{ mol}^{-1}$ , and that the quantity  $23,070 \text{ cal volt}^{-1} \text{ mol}^{-1} \text{ faraday}^{-1}$  is dimensionless and equal to unity.
7. If an electric motor produces 10 kJ of energy per second as work and dispenses 2 kJ of energy as heat to the surroundings. Calculate the change in internal energy of the electric motor per second.
8. A spring is wound by investing 50 kJ of energy as mechanical work and during that process 5 kJ of energy was lost to the surrounding as heat. Calculate the change in internal energy of the spring.
9. Calculate the work done when 100 g of calcium carbonate dissociates completely into calcium oxide and carbon dioxide (a) in a closed vessel of constant volume, (b) in vacuum and (c) in an open beaker at  $25^\circ\text{C}$ .
10. Calculate the work done when 58 g of gaseous butane burns completely in the presence of oxygen in an open atmosphere. Express your result as a function of T.

**First Law of Thermodynamics**

11. Calculate the difference in the change in enthalpy and the change in internal energy of one mole of Sn(s, grey) of densities 5.75 g cc<sup>-1</sup> converts in to Sn(s, white) of density 7.31 g cc<sup>-1</sup> at 10 bar pressure at 298 K.
12. Calculate the difference in the change in enthalpy and the change in internal energy of one mole of C(s, graphite) of densities **2.26** g cc<sup>-1</sup> converts in to C(s, diamond) of density **3.51** g cc<sup>-1</sup> at 1000 bar pressure at 1500 K.
13. Water is heated to boiling through an electric heater in thermal contact with it. A current of 1 A from a supply of 12 V is passed for 2.5 min, under a pressure of 1.0 atm. It was observed that 800 mg of water is vaporized. Calculate the change in molar enthalpy and change in molar internal energy during evaporation. [40.5 kJ mol<sup>-1</sup>, 37.5 kJ mol<sup>-1</sup>]
14. The boiling point and molar enthalpy of vaporization of benzene are 80 °C and 30.8 kJ mol<sup>-1</sup>. In order to vaporize 10 g of benzene, how long it would require to supply a current of 0.5 A from a 12 V source? Calculate the change in molar internal energy. [27.9 kJ mol<sup>-1</sup>, 660 s]
15. The Debye extrapolation provides the dependability of the heat capacity for a solid at extremely low temperature which can be written as  $C_p = aT^3$ . A sample of solid is heated from a temperature close to 0 K to a temperature T, calculate the change in enthalpy.
16. Calculate the difference between final pressures of a sample of argon ( $\gamma = 5/3$ ) at 200 kPa expands in an isothermal reversible and in a reversible adiabatic processes to thrice of its initial volume.
17. From the equation of state  $PV = nRT$  for an ideal gas, show that the volume expansivity is equal to  $1/T$  and isothermal compressibility is equal to  $1/P$ .
18. A reaction occurs in a vessel fitted with a movable piston of cross-sectional area 40 cm<sup>2</sup>. After completion of reaction, the piston is driven outwardly by 10 cm against an external pressure of 100 kPa. Calculate the work done by the system.
19. A sample of gas Ar expands isothermally at 0 °C to double of its volume (a) freely, against zero external pressure (b) reversibly and (c) against a constant external pressure which may be treated as equivalent to the final pressure of the gas. For three processes calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .
20. Calculate the final pressure,  $q$ ,  $w$  and  $\Delta U$  for a one mole of a monatomic perfect gas initially at 1.0 atm and 300 K, when heated to a temperature of 400 K at constant volume.

**First Law of Thermodynamics**

21. At 37 °C, a sample of 6.0 g of ethane gas occupies a volume of 15 dm<sup>3</sup>. Calculate the work done when the gas expands isothermally (a) against a constant external pressure of 500 torr until its volume has increased by 4.5 dm<sup>3</sup>. (b) If the expansion has occurred reversibly.
22. When a sample of helium (for which  $\gamma = 3R/2$ ) at 100 kPa expands reversibly and adiabatically to thrice of its initial volume. Calculate the final pressure.
23. The expression  $C_p / (J K^{-1}) = 20.17 + 0.3665(T/K)$  show the variation of constant-pressure heat capacity of a sample of a perfect gas with temperature. The temperature of the sample was raised from 25 to 200 °C (a) at constant pressure (b) at constant volume, calculate the  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$ .
24. 12 g of a sample of argon expands reversibly and adiabatically from 1 to 3 dm<sup>3</sup> at 0 °C, calculate the final pressure of the sample.
25. A sample of 4.4 g carbon dioxide undergoes reversible adiabatic expansion at 300 K from a volume of 500 cc to 3.0 dm<sup>3</sup>. Calculate the work done by the gas.
26. An increase in the temperature of a sample of 3.0 mol argon (gas) was found to be of 3 K when 277 J of energy was supplied as heat. Calculate the molar heat capacities of the gas at constant pressure and constant volume.
27. Calculate  $q$ ,  $\Delta U$  and  $\Delta H$ , when a sample of a 2.0 mol of carbon dioxide is heated from 240 to 280 K at a constant pressure of 1.25 atm. Given that  $C_{p,CO_2} = 37.11 J K^{-1} mol^{-1}$ .
28. A fall of 10 K temperature was observed when a vapor at 25 atm and 278 K is allowed to expand to a final pressure of 1.0 atm adiabatically. Calculate the J-T coefficient,  $\mu$  at 278 K. assuming that  $\mu$  does not vary in this temperature range.
29. The volume of a particular liquid depends on temperature as  $V_T = V_0\{0.77 + 3.7 \times 10^{-4} (T-298) + 1.52 \times 10^{-6} (T-298)^2\}$ , where  $V_0$  is the volume at 298 K. Calculate the coefficient of expansion,  $\alpha$  at 320 K.
30. Calculate the pressure that needs to be applied in order to increase the density of lead by 0.08 percent if its isothermal compressibility at 293 K is  $2.21 \times 10^{-6} atm^{-1}$ .

**GOOD LUCK**

*NOTE: Sources: P. W. Atkins, Glasstone, Laidler & Meiser*