

Exercises

Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.

3.1(a) Calculate the change in entropy when 25 kJ of energy is transferred reversibly and isothermally as heat to a large block of iron at (a) 0°C, (b) 100°C.

3.1(b) Calculate the change in entropy when 50 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0°C, (b) 70°C.

3.2(a) Calculate the molar entropy of a constant-volume sample of neon at 500 K given that it is $146.22 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K.

3.2(b) Calculate the molar entropy of a constant-volume sample of argon at 250 K given that it is $154.84 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K.

3.3(a) Calculate ΔS (for the system) when the state of 3.00 mol of perfect gas atoms, for which $C_{p,m} = \frac{5}{2}R$, is changed from 25°C and 1.00 atm to 125°C and 5.00 atm. How do you rationalize the sign of ΔS ?

3.3(b) Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m} = \frac{7}{2}R$, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS ?

3.4(a) A sample consisting of 3.00 mol of diatomic perfect gas molecules at 200 K is compressed reversibly and adiabatically until its temperature reaches 250 K. Given that $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS .

3.4(b) A sample consisting of 2.00 mol of diatomic perfect gas molecules at 250 K is compressed reversibly and adiabatically until its temperature reaches 300 K. Given that $C_{V,m} = 27.5 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate q , w , ΔU , ΔH , and ΔS .

3.5(a) Calculate ΔH and ΔS_{tot} when two copper blocks, each of mass 10.0 kg, one at 100°C and the other at 0°C, are placed in contact in an isolated container. The specific heat capacity of copper is $0.385 \text{ J K}^{-1} \text{ g}^{-1}$ and may be assumed constant over the temperature range involved.

3.5(b) Calculate ΔH and ΔS_{tot} when two iron blocks, each of mass 1.00 kg, one at 200°C and the other at 25°C, are placed in contact in an isolated container. The specific heat capacity of iron is $0.449 \text{ J K}^{-1} \text{ g}^{-1}$ and may be assumed constant over the temperature range involved.

3.6(a) Consider a system consisting of 2.0 mol $\text{CO}_2(\text{g})$, initially at 25°C and 10 atm and confined to a cylinder of cross-section 10.0 cm^2 . It is allowed to expand adiabatically against an external pressure of 1.0 atm until the piston has moved outwards through 20 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , (e) ΔS .

3.6(b) Consider a system consisting of 1.5 mol $\text{CO}_2(\text{g})$, initially at 15°C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2 . The sample is allowed to expand adiabatically against an external pressure of 1.5 atm until the piston has moved outwards through 15 cm. Assume that carbon dioxide may be considered a perfect gas with $C_{V,m} = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$, and calculate (a) q , (b) w , (c) ΔU , (d) ΔT , (e) ΔS .

3.7(a) The enthalpy of vaporization of chloroform (CHCl_3) is 29.4 kJ mol^{-1} at its normal boiling point of 334.88 K. Calculate (a) the entropy of vaporization of chloroform at this temperature and (b) the entropy change of the surroundings.

3.7(b) The enthalpy of vaporization of methanol is $35.27 \text{ kJ mol}^{-1}$ at its normal boiling point of 64.1°C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

3.8(a) Calculate the standard reaction entropy at 298 K of

- (a) $2 \text{ CH}_3\text{CHO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ CH}_3\text{COOH}(\text{l})$
- (b) $2 \text{ AgCl}(\text{s}) + \text{Br}_2(\text{l}) \rightarrow 2 \text{ AgBr}(\text{s}) + \text{Cl}_2(\text{g})$
- (c) $\text{Hg}(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{HgCl}_2(\text{s})$

3.8(b) Calculate the standard reaction entropy at 298 K of

- (a) $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
- (b) $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 12 \text{ O}_2(\text{g}) \rightarrow 12 \text{ CO}_2(\text{g}) + 11 \text{ H}_2\text{O}(\text{l})$

3.9(a) Combine the reaction entropies calculated in Exercise 3.8a with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3.9(b) Combine the reaction entropies calculated in Exercise 3.8b with the reaction enthalpies, and calculate the standard reaction Gibbs energies at 298 K.

3.10(a) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8a.

3.10(b) Use standard Gibbs energies of formation to calculate the standard reaction Gibbs energies at 298 K of the reactions in Exercise 3.8b.

3.11(a) Calculate the standard Gibbs energy of the reaction $4 \text{ HCl}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ Cl}_2(\text{g}) + 2 \text{ H}_2\text{O}(\text{l})$ at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

3.11(b) Calculate the standard Gibbs energy of the reaction $\text{CO}(\text{g}) + \text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{COOH}(\text{l})$ at 298 K, from the standard entropies and enthalpies of formation given in the *Data section*.

3.12(a) The standard enthalpy of combustion of solid phenol ($\text{C}_6\text{H}_5\text{OH}$) is $-3054 \text{ kJ mol}^{-1}$ at 298 K and its standard molar entropy is $144.0 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of phenol at 298 K.

3.12(b) The standard enthalpy of combustion of solid urea ($\text{CO}(\text{NH}_2)_2$) is -632 kJ mol^{-1} at 298 K and its standard molar entropy is $104.60 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the standard Gibbs energy of formation of urea at 298 K.

3.13(a) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K and 1.00 bar doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

3.13(b) Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 21 g at 298 K and 1.50 bar increases from 1.20 dm^3 to 4.60 dm^3 in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{\text{ex}} = 0$, and (c) an adiabatic reversible expansion.

3.14(a) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of methane at 298 K.

3.14(b) Calculate the maximum non-expansion work per mole that may be obtained from a fuel cell in which the chemical reaction is the combustion of propane at 298 K.

3.15(a) (a) Calculate the Carnot efficiency of a primitive steam engine operating on steam at 100°C and discharging at 60°C. (b) Repeat the calculation for a modern steam turbine that operates with steam at 300°C and discharges at 80°C.

3.15(b) A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done by for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

3.16(a) Suppose that 3.0 mmol $\text{N}_2(\text{g})$ occupies 36 cm^3 at 300 K and expands to 60 cm^3 . Calculate ΔG for the process.

3.16(b) Suppose that 2.5 mmol $\text{Ar}(\text{g})$ occupies 72 dm^3 at 298 K and expands to 100 dm^3 . Calculate ΔG for the process.

3.17(a) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\text{J} = -85.40 + 36.5(T/\text{K})$. Calculate the value of ΔS for the process.

3.17(b) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\text{J} = -73.1 + 42.8(T/\text{K})$. Calculate the value of ΔS for the process.

3.18(a) Calculate the change in Gibbs energy of 35 g of ethanol (mass density 0.789 g cm^{-3}) when the pressure is increased isothermally from 1 atm to 3000 atm.

3.18(b) Calculate the change in Gibbs energy of 25 g of methanol (mass density 0.791 g cm^{-3}) when the pressure is increased isothermally from 100 kPa to 100 MPa.

3.19(a) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 1.8 atm to 29.5 atm at 40°C .

3.19(b) Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 92.0 kPa to 252.0 kPa at 50°C .

3.20(a) The fugacity coefficient of a certain gas at 200 K and 50 bar is 0.72. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

3.20(b) The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.

3.21(a) Estimate the change in the Gibbs energy of 1.0 dm^3 of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

3.21(b) Estimate the change in the Gibbs energy of 1.0 dm^3 of water when the pressure acting on it is increased from 100 kPa to 300 kPa.

3.22(a) Calculate the change in the molar Gibbs energy of hydrogen gas when its pressure is increased isothermally from 1.0 atm to 100.0 atm at 298 K.

3.22(b) Calculate the change in the molar Gibbs energy of oxygen when its pressure is increased isothermally from 50.0 kPa to 100.0 kPa at 500 K.

Problems*

Assume that all gases are perfect and that data refer to 298 K unless otherwise stated.

Numerical problems

3.1 Calculate the difference in molar entropy (a) between liquid water and ice at -5°C , (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are $37.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-41.9 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

3.2 The heat capacity of chloroform (trichloromethane, CHCl_3) in the range 240 K to 330 K is given by $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = 91.47 + 7.5 \times 10^{-2} (T/\text{K})$. In a particular experiment, 1.00 mol CHCl_3 is heated from 273 K to 300 K. Calculate the change in molar entropy of the sample.

3.3 A block of copper of mass 2.00 kg ($C_{p,m} = 24.44 \text{ J K}^{-1} \text{ mol}^{-1}$) and temperature 0°C is introduced into an insulated container in which there is 1.00 mol $\text{H}_2\text{O}(\text{g})$ at 100°C and 1.00 atm. (a) Assuming all the steam is condensed to water, what will be the final temperature of the system, the heat transferred from water to copper, and the entropy change of the water, copper, and the total system? (b) In fact, some water vapour is present at equilibrium. From the vapour pressure of water at the temperature calculated in (a), and assuming that the heat capacities of both gaseous and liquid water are constant and given by their values at that temperature, obtain an improved value of the final temperature, the heat transferred, and the various entropies. (Hint. You will need to make plausible approximations.)

3.4 Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections A and B. All changes in B is isothermal; that is, a thermostat surrounds B to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially, $T_A = T_B = 300 \text{ K}$, $V_A = V_B$

$= 2.00 \text{ dm}^3$. Energy is supplied as heat to Section A and the piston moves to the right reversibly until the final volume of Section B is 1.00 dm^3 . Calculate (a) ΔS_A and ΔS_B , (b) ΔA_A and ΔA_B , (c) ΔG_A and ΔG_B , (d) ΔS of the total system and its surroundings. If numerical values cannot be obtained, indicate whether the values should be positive, negative, or zero or are indeterminate from the information given. (Assume $C_{V,m} = 20 \text{ J K}^{-1} \text{ mol}^{-1}$.)

3.5 A Carnot cycle uses 1.00 mol of a monatomic perfect gas as the working substance from an initial state of 10.0 atm and 600 K. It expands isothermally to a pressure of 1.00 atm (Step 1), and then adiabatically to a temperature of 300 K (Step 2). This expansion is followed by an isothermal compression (Step 3), and then an adiabatic compression (Step 4) back to the initial state. Determine the values of q , w , ΔU , ΔH , ΔS , ΔS_{tot} , and ΔG for each stage of the cycle and for the cycle as a whole. Express your answer as a table of values.

3.6 1.00 mol of perfect gas molecules at 27°C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Determine the values of q , w , ΔU , ΔH , ΔS , ΔS_{sur} , ΔS_{tot} for each path.

3.7 The standard molar entropy of $\text{NH}_3(\text{g})$ is $192.45 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K, and its heat capacity is given by eqn 2.25 with the coefficients given in Table 2.2. Calculate the standard molar entropy at (a) 100°C and (b) 500°C .

3.8 A block of copper of mass 500 g and initially at 293 K is in thermal contact with an electric heater of resistance $1.00 \text{ k}\Omega$ and negligible mass. A current of 1.00 A is passed for 15.0 s. Calculate the change in entropy of the copper, taking $C_{p,m} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$. The experiment is then repeated with the copper immersed in a stream of water that maintains its temperature at 293 K. Calculate the change in entropy of the copper and the water in this case.

3.9 Find an expression for the change in entropy when two blocks of the same substance and of equal mass, one at the temperature T_h and the other at T_c , are brought into thermal contact and allowed to reach equilibrium. Evaluate the

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

change for two blocks of copper, each of mass 500 g, with $C_{p,m} = 24.4 \text{ J K}^{-1} \text{ mol}^{-1}$, taking $T_h = 500 \text{ K}$ and $T_c = 250 \text{ K}$.

3.10 A gaseous sample consisting of 1.00 mol molecules is described by the equation of state $pV_m = RT(1 + Bp)$. Initially at 373 K, it undergoes Joule–Thomson expansion from 100 atm to 1.00 atm. Given that $C_{p,m} = \frac{5}{2}R$, $\mu = 0.21 \text{ K atm}^{-1}$, $B = -0.525(\text{K/T}) \text{ atm}^{-1}$, and that these are constant over the temperature range involved, calculate ΔT and ΔS for the gas.

3.11 The molar heat capacity of lead varies with temperature as follows:

T/K	10	15	20	25	30	50
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	2.8	7.0	10.8	14.1	16.5	21.4
T/K	70	100	150	200	250	298
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	23.3	24.5	25.3	25.8	26.2	26.6

Calculate the standard Third-Law entropy of lead at (a) 0°C and (b) 25°C .

3.12 From standard enthalpies of formation, standard entropies, and standard heat capacities available from tables in the *Data section*, calculate the standard enthalpies and entropies at 298 K and 398 K for the reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$. Assume that the heat capacities are constant over the temperature range involved.

3.13 The heat capacity of anhydrous potassium hexacyanoferrate(II) varies with temperature as follows:

T/K	$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	T/K	$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$
10	2.09	100	179.6
20	14.43	110	192.8
30	36.44	150	237.6
40	62.55	160	247.3
50	87.03	170	256.5
60	111.0	180	265.1
70	131.4	190	273.0
80	149.4	200	280.3
90	165.3		

Calculate the molar enthalpy relative to its value at $T = 0$ and the Third-Law entropy at each of these temperatures.

3.14 The compound 1,3,5-trichloro-2,4,6-trifluorobenzene is an intermediate in the conversion of hexachlorobenzene to hexafluorobenzene, and its thermodynamic properties have been examined by measuring its heat capacity over a wide temperature range (R.L. Andon and J.F. Martin, *J. Chem. Soc. Faraday Trans. I*, 871 (1973)). Some of the data are as follows:

T/K	14.14	16.33	20.03	31.15	44.08	64.81
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	9.492	12.70	18.18	32.54	46.86	66.36
T/K	100.90	140.86	183.59	225.10	262.99	298.06
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	95.05	121.3	144.4	163.7	180.2	196.4

Calculate the molar enthalpy relative to its value at $T = 0$ and the Third-Law molar entropy of the compound at these temperatures.

3.15† Given that $S_m^\circ = 29.79 \text{ J K}^{-1} \text{ mol}^{-1}$ for bismuth at 100 K and the following tabulated heat capacities data (D.G. Archer, *J. Chem. Eng. Data* **40**, 1015 (1995)), compute the standard molar entropy of bismuth at 200 K.

T/K	100	120	140	150	160	180	200
$C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1})$	23.00	23.74	24.25	24.44	24.61	24.89	25.11

Compare the value to the value that would be obtained by taking the heat capacity to be constant at $24.44 \text{ J K}^{-1} \text{ mol}^{-1}$ over this range.

3.16 Calculate $\Delta_r G^\circ(375 \text{ K})$ for the reaction $2 \text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{CO}_2(\text{g})$ from the value of $\Delta_r G^\circ(298 \text{ K})$, $\Delta_r H^\circ(298 \text{ K})$, and the Gibbs–Helmholtz equation.

3.17 Estimate the standard reaction Gibbs energy of $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ at (a) 500 K, (b) 1000 K from their values at 298 K.

3.18 At 200 K, the compression factor of oxygen varies with pressure as shown below. Evaluate the fugacity of oxygen at this temperature and 100 atm.

p/atm	1.0000	4.00000	7.00000	10.0000	40.00	70.00	100.0
Z	0.9971	0.98796	0.97880	0.96956	0.8734	0.7764	0.6871

Theoretical problems

3.19 Represent the Carnot cycle on a temperature–entropy diagram and show that the area enclosed by the cycle is equal to the work done.

3.20 Prove that two reversible adiabatic paths can never cross. Assume that the energy of the system under consideration is a function of temperature only. (*Hint*. Suppose that two such paths can intersect, and complete a cycle with the two paths plus one isothermal path. Consider the changes accompanying each stage of the cycle and show that they conflict with the Kelvin statement of the Second Law.)

3.21 Prove that the perfect gas temperature scale and the thermodynamic temperature scale based on the Second Law of thermodynamics differ from each other by at most a constant numerical factor.

3.22 The molar Gibbs energy of a certain gas is given by $G_m = RT \ln p + A + Bp + \frac{1}{2}Cp^2 + \frac{1}{3}Dp^3$, where A , B , C , and D are constants. Obtain the equation of state of the gas.

3.23 Evaluate $(\partial S/\partial V)_T$ for (a) a van der Waals gas, (b) a Dieterici gas (Table 1.7). For an isothermal expansion, for which kind of gas (and a perfect gas) will ΔS be greatest? Explain your conclusion.

3.24 Show that, for a perfect gas, $(\partial U/\partial S)_V = T$ and $(\partial U/\partial V)_S = -p$.

3.25 Two of the four Maxwell relations were derived in the text, but two were not. Complete their derivation by showing that $(\partial S/\partial V)_T = (\partial p/\partial T)_V$ and $(\partial T/\partial p)_S = (\partial V/\partial S)_p$.

3.26 Use the Maxwell relations to express the derivatives (a) $(\partial S/\partial V)_T$ and $(\partial V/\partial S)_p$ and (b) $(\partial p/\partial S)_V$ and $(\partial V/\partial S)_p$ in terms of the heat capacities, the expansion coefficient α , and the isothermal compressibility, κ_T .

3.27 Use the Maxwell relations to show that the entropy of a perfect gas depends on the volume as $S \propto R \ln V$.

3.28 Derive the thermodynamic equation of state

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$$

Derive an expression for $(\partial H/\partial p)_T$ for (a) a perfect gas and (b) a van der Waals gas. In the latter case, estimate its value for 1.0 mol Ar(g) at 298 K and 10 atm. By how much does the enthalpy of the argon change when the pressure is increased isothermally to 11 atm?

3.29 Show that if $B(T)$ is the second virial coefficient of a gas, and $\Delta B = B(T'') - B(T')$, $\Delta T = T'' - T'$, and T is the mean of T'' and T' , then $\pi_T \approx RT^2 \Delta B/V_m^2 \Delta T$. Estimate π_T for argon given that $B(250 \text{ K}) = -28.0 \text{ cm}^3 \text{ mol}^{-1}$ and $B(300 \text{ K}) = -15.6 \text{ cm}^3 \text{ mol}^{-1}$ at 275 K at (a) 1.0 atm, (b) 10.0 atm.

3.30 The Joule coefficient, μ_J , is defined as $\mu_J = (\partial T/\partial V)_U$. Show that $\mu_J C_V = p - \alpha T/\kappa_T$.

3.31 Evaluate π_T for a Dieterici gas (Table 1.7). Justify physically the form of the expression obtained.

3.32 The adiabatic compressibility, κ_S , is defined like κ_T (eqn 2.44) but at constant entropy. Show that for a perfect gas $p\gamma\kappa_S = 1$ (where γ is the ratio of heat capacities).