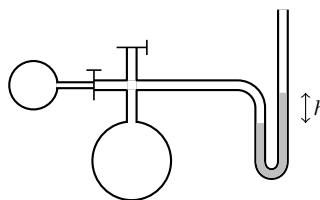


2 The First and Second Laws of Thermodynamics

- 2/8: 1. Consider the following experiment with an ideal gas, and derive the relation between γ , h , and h' .

Let the system sit at P_0, T_0 where $h = 0$. Pump a little gas in (add Δn) and wait so that T is back to T_0 ; measure h . Open the valve to air quickly to P_0 and close again. Justify why this can be considered a reversible adiabatic expansion. Wait so that T is back to T_0 ; measure h' .



2. (a) n moles of an ideal gas with a given γ undergo an adiabatic expansion from V_a to V_b . Calculate the work done and the total energy change.
- (b) n moles of an ideal gas with a given γ undergo an isobaric expansion from V_a to V_b . Calculate the work done and the total energy change.
3. (a) Consider a Carnot cycle for an ideal gas. Derive the relation $Q_1/T_1 + Q_2/T_2 = 0$ where Q_1, Q_2 are the heat transferred to the system along the isotherms at T_1, T_2 .
- (b) Consider an ideal gas going from V_1, T_1 to V_2, T_2 . Calculate the entropy change in terms of V_1, V_2, T_2, T_1 .
4. Practicing with partial derivatives.

By expressing the internal energy state function U in terms of V and T variables and alternatively with P and T variables, show that

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \quad \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial U}{\partial V}\right)_T$$

Then derive that

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P$$

Show that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

for an ideal gas. And then show that

$$C_P - C_V = nR$$

5. Write that $dU = T dS - P dV$ and derive the following two relations.

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

6. Problem 21-10. Show your work.

It has been found experimentally that $\Delta_{\text{vap}} \bar{S} \approx 88 \text{ J K}^{-1} \text{ mol}^{-1}$ for many nonassociated liquids. This rough rule of thumb is called **Trouton's rule**. Use the following data to test the validity of Trouton's rule.

Substance	$t_{\text{fus}}/^{\circ}\text{C}$	$t_{\text{vap}}/^{\circ}\text{C}$	$\Delta_{\text{fus}}\overline{H}/\text{kJ mol}^{-1}$	$\Delta_{\text{vap}}\overline{H}/\text{kJ mol}^{-1}$
Pentane	-129.7	36.06	8.42	25.79
Hexane	-95.3	68.73	13.08	28.85
Heptane	-90.6	98.5	14.16	31.77
Ethylene oxide	-111.7	10.6	5.17	25.52
Benzene	5.53	80.09	9.95	30.72
Diethyl ether	-116.3	34.5	7.27	26.52
Tetrachloromethane	-23	76.8	3.28	29.82
Mercury	-38.83	356.7	2.29	59.11
Bromine	-7.2	58.8	10.57	29.96

7. Problem 21-37. Show your reasoning.

Given that $\tilde{\nu}_1 = 1321.3 \text{ cm}^{-1}$, $\tilde{\nu}_2 = 750.8 \text{ cm}^{-1}$, $\tilde{\nu}_3 = 1620.3 \text{ cm}^{-1}$, $\tilde{A}_0 = 7.9971 \text{ cm}^{-1}$, $\tilde{B}_0 = 0.4339 \text{ cm}^{-1}$, and $\tilde{C}_0 = 0.4103 \text{ cm}^{-1}$, calculate the standard molar entropy of $\text{NO}_{2(\text{g})}$ at 298.15 K. (Note that $\text{NO}_{2(\text{g})}$ is a bent triatomic molecule.) How does your value compare with that in Table 21.2?

8. Problem 19-55.

Use the rigid rotator-harmonic oscillator model and the data in Table 18.2 to plot $\overline{C}_P(T)$ for $\text{CO}_{(\text{g})}$ from 300 K to 1000 K. Compare your result with the expression given in Problem 19-43.