

Homework CH2

Exercise

2A.4(b) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

(i) $\Delta U = \Delta H = 0$

$$w = -nRT \ln \left(\frac{V_f}{V_i} \right) \quad [2A.9]$$

$$= -(2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times 273 \text{ K} \times \ln \frac{20.0 \text{ dm}^3}{5.0 \text{ dm}^3} = \boxed{-6.29 \times 10^3 \text{ J}}$$

$$q = -w = \boxed{6.29 \times 10^3 \text{ J}}$$

(ii) $\Delta U = \Delta H = 0$

$$w = -p_{\text{ex}} \Delta V \quad [2A.6]$$

where p_{ex} in this case can be computed from the perfect gas law

$$pV = nRT$$

$$\text{so } p = \frac{(2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times 273 \text{ K}}{20.0 \text{ dm}^3} \times (10 \text{ dm m}^{-1})^3 = 2.22 \times 10^5 \text{ Pa}$$

$$\text{and } w = \frac{-(2.22 \times 10^5 \text{ Pa}) \times (20.0 - 5.0) \text{ dm}^3}{(10 \text{ dm m}^{-1})^3} = \boxed{-3.34 \times 10^3 \text{ J}}$$

$$q = -w = \boxed{3.34 \times 10^3 \text{ J}}$$

(iii) $\Delta U = \Delta H = 0$

$$\boxed{w = 0} \quad [\text{free expansion}] \quad q = \Delta U - w = 0 - 0 = \boxed{0}$$

Comment. An isothermal free expansion of a perfect gas is also adiabatic.

2B.2(b) (i) At constant pressure, $q = \Delta H$.

$$q = \int C_p dT = \int_{25+273\text{K}}^{100+273\text{K}} [20.17 + (0.4001)T / \text{K}] dT \text{ J K}^{-1}$$

$$= \left[(20.17)T + \frac{1}{2}(0.4001) \times \left(\frac{T^2}{\text{K}} \right) \right]_{298\text{K}}^{373\text{K}} \text{ J K}^{-1}$$

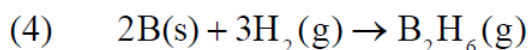
$$= \left[(20.17) \times (373 - 298) + \frac{1}{2}(0.4001) \times (373^2 - 298^2) \right] \text{ J} = \boxed{11.6 \times 10^3 \text{ J}} = \Delta H$$

$$w = -p\Delta V = -nR\Delta T = -(1.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (75 \text{ K}) = \boxed{-623 \text{ J}}$$

$$\Delta U = q + w = (11.6 - 0.623) \text{ kJ} = \boxed{11.0 \text{ kJ}}$$

(ii) The energy and enthalpy of a perfect gas depend on temperature alone. Thus, $\Delta H = \boxed{11.6 \text{ kJ}}$ and $\Delta U = \boxed{11.0 \text{ kJ}}$, as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+11.0 \text{ kJ}}$.

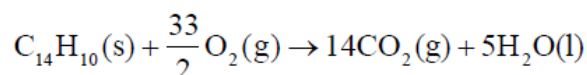
2C.3(b) We need $\Delta_f H^\ominus$ for the reaction



$$\text{reaction(4)} = \text{reaction(2)} + 3 \times \text{reaction(3)} - \text{reaction(1)}$$

$$\begin{aligned} \text{Thus, } \Delta_f H^\ominus &= \Delta_r H^\ominus \{\text{reaction(2)}\} + 3 \times \Delta_r H^\ominus \{\text{reaction(3)}\} - \Delta_r H^\ominus \{\text{reaction(1)}\} \\ &= [-1274 + 3 \times (-241.8) - (-2036)] \text{ kJ mol}^{-1} = \boxed{+36.6 \text{ kJ mol}^{-1}} \end{aligned}$$

2C.5(b) For anthracene the reaction is



$$\Delta_c U^\ominus = \Delta_c H^\ominus - \Delta n_g RT \text{ [2B.4]}, \quad \Delta n_g = -\frac{5}{2} \text{ mol}$$

$$\begin{aligned} \Delta_c U^\ominus &= -7061 \text{ kJ mol}^{-1} - \left(-\frac{5}{2} \times 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \right) \\ &= -7055 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} |q| = |q_v| &= |n \Delta_c U^\ominus| = \left(\frac{225 \times 10^{-3} \text{ g}}{178.23 \text{ g mol}^{-1}} \right) \times (7055 \text{ kJ mol}^{-1}) \\ &= 8.91 \text{ kJ} \end{aligned}$$

$$C = \frac{|q|}{\Delta T} = \frac{8.91 \text{ kJ}}{1.35 \text{ K}} = \boxed{6.60 \text{ kJ K}^{-1}}$$

When phenol is used the reaction is $\text{C}_6\text{H}_5\text{OH}(\text{s}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

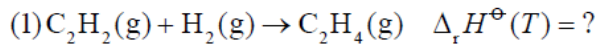
$$\Delta_c H^\ominus = -3054 \text{ kJ mol}^{-1} \text{ [Table 2C.1]}$$

$$\begin{aligned} \Delta_c U &= \Delta_c H - \Delta n_g RT, \quad \Delta n_g = -\frac{3}{2} \\ &= (-3054 \text{ kJ mol}^{-1}) + \left(\frac{3}{2} \right) \times (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \\ &= -3050 \text{ kJ mol}^{-1} \end{aligned}$$

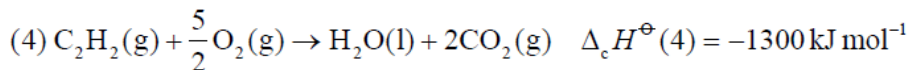
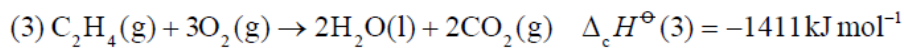
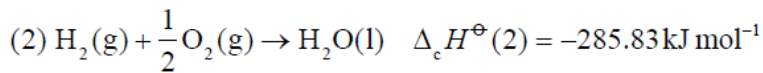
$$|q| = \left(\frac{135 \times 10^{-3} \text{ g}}{94.12 \text{ g mol}^{-1}} \right) \times (3050 \text{ kJ mol}^{-1}) = 4.375 \text{ kJ}$$

$$\Delta T = \frac{|q|}{C} = \frac{4.375 \text{ kJ}}{6.60 \text{ kJ K}^{-1}} = \boxed{+0.663 \text{ K}}$$

2C.8(b) The hydrogenation reaction is



The reactions and accompanying data which are to be combined in order to yield reaction (1) and $\Delta_r H^\ominus(T)$ are



$$\text{reaction (1)} = \text{reaction (2)} - \text{reaction (3)} + \text{reaction (4)}$$

Hence, at 298 K:

$$\begin{aligned} \Delta_r H^\ominus &= \Delta_c H^\ominus(2) - \Delta_c H^\ominus(3) + \Delta_c H^\ominus(4) \\ \text{(i)} \quad &= [(-285.83) - (-1411) + (-1300)] \text{ kJ mol}^{-1} = \boxed{-175 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\begin{aligned} \Delta_r U^\ominus &= \Delta_r H^\ominus - \Delta n_g RT \quad [2B.4]; \quad \Delta n_g = -1 \\ &= -175 \text{ kJ mol}^{-1} - (-1) \times (2.48 \text{ kJ mol}^{-1}) = \boxed{-173 \text{ kJ mol}^{-1}} \end{aligned}$$

(ii) At 427 K:

$$\Delta_r H^\ominus(427 \text{ K}) = \Delta_r H^\ominus(298 \text{ K}) + \Delta_r C_p^\ominus(427 \text{ K} - 298 \text{ K}) \quad [\text{Example 2C.2}]$$

$$\begin{aligned} \Delta_r C_p &= \sum_J \nu_J C_{p,m}^\ominus(J) [2C.7c] = C_{p,m}^\ominus(\text{C}_2\text{H}_4, \text{g}) - C_{p,m}^\ominus(\text{C}_2\text{H}_2, \text{g}) - C_{p,m}^\ominus(\text{H}_2, \text{g}) \\ &= (43.56 - 43.93 - 28.82) \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} = -29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_r H^\ominus(427 \text{ K}) &= (-175 \text{ kJ mol}^{-1}) - (29.19 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \times (129 \text{ K}) \\ &= \boxed{-171 \text{ kJ mol}^{-1}} \end{aligned}$$

2D.2(b) The internal energy is a function of temperature and volume, $U_m = U_m(T, V_m)$, so

$$dU_m = \left(\frac{\partial U_m}{\partial T} \right)_{V_m} dT + \left(\frac{\partial U_m}{\partial V_m} \right)_T dV_m \quad [\pi_T = (\partial U_m / \partial V)_T]$$

For an isothermal expansion $dT = 0$; hence

$$dU_m = \left(\frac{\partial U_m}{\partial V_m} \right)_T dV_m = \pi_T dV_m = \frac{a}{V_m^2} dV_m$$

$$\begin{aligned} \Delta U_m &= \int_{V_{m1}}^{V_{m2}} dU_m = \int_{V_{m2}}^{V_{m1}} \frac{a}{V_m^2} dV_m = a \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{30.00 \text{ dm}^3 \text{ mol}^{-1}} \frac{dV_m}{V_m^2} = -\frac{a}{V_m} \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{30.00 \text{ dm}^3 \text{ mol}^{-1}} \\ &= -\frac{a}{30.00 \text{ dm}^3 \text{ mol}^{-1}} + \frac{a}{1.00 \text{ dm}^3 \text{ mol}^{-1}} = \frac{29.00a}{30.00 \text{ dm}^3 \text{ mol}^{-1}} = 0.9667a \text{ dm}^{-3} \text{ mol} \end{aligned}$$

From Table 1C.3, $a = 1.337 \text{ dm}^6 \text{ atm mol}^{-1}$

$$\begin{aligned} \Delta U_m &= (0.9667 \text{ mol dm}^3) \times (1.337 \text{ atm dm}^6 \text{ mol}^{-2}) \\ &= (1.2924 \text{ atm dm}^3 \text{ mol}^{-1}) \times (1.01325 \times 10^5 \text{ Pa atm}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ dm}^3} \right) \\ &= 131.0 \text{ Pa m}^3 \text{ mol}^{-1} = \boxed{131.0 \text{ J mol}^{-1}} \end{aligned}$$

$$w = -\int p dV_m \quad \text{where} \quad p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad \text{for a van der Waals gas. Hence,}$$

$$w = -\int \left(\frac{RT}{V_m - b} \right) dV_m + \int \frac{a}{V_m^2} dV_m = -q + \Delta U_m$$

Thus

$$\begin{aligned} q &= \int_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{30.00 \text{ dm}^3 \text{ mol}^{-1}} \left(\frac{RT}{V_m - b} \right) dV_m = RT \ln(V_m - b) \Big|_{1.00 \text{ dm}^3 \text{ mol}^{-1}}^{30.00 \text{ dm}^3 \text{ mol}^{-1}} \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln \left(\frac{30.00 - 3.20 \times 10^{-2}}{1.00 - 3.20 \times 10^{-2}} \right) = \boxed{+8.505 \text{ kJ mol}^{-1}} \end{aligned}$$

$$\text{and } w = -q + \Delta U_m = -(8505 \text{ J mol}^{-1}) + (131 \text{ J mol}^{-1}) = \boxed{-8374 \text{ J mol}^{-1}} = \boxed{-8.37 \text{ kJ mol}^{-1}}$$

2D.3(b) The expansion coefficient is

$$\begin{aligned}\alpha &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{V'(3.7 \times 10^{-4} \text{ K}^{-1} + 2 \times 1.52 \times 10^{-6} T \text{ K}^{-2})}{V} \\ &= \frac{V'[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (T / \text{K})] \text{ K}^{-1}}{V[0.77 + 3.7 \times 10^{-4} (T / \text{K}) + 1.52 \times 10^{-6} (T / \text{K})^2]} \\ &= \frac{[3.7 \times 10^{-4} + 2 \times 1.52 \times 10^{-6} (310)] \text{ K}^{-1}}{0.77 + 3.7 \times 10^{-4} (310) + 1.52 \times 10^{-6} (310)^2} = \boxed{1.27 \times 10^{-3} \text{ K}^{-1}}\end{aligned}$$

2D.4(b) Isothermal compressibility is

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \approx -\frac{\Delta V}{V \Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V \kappa_T}$$

A density increase of 0.10 per cent means $\Delta V / V = -0.0010$. So the additional pressure that must be applied is

$$\Delta p = \frac{0.0010}{2.21 \times 10^{-6} \text{ atm}^{-1}} = \boxed{4.5 \times 10^2 \text{ atm}}$$

2D.5(b) The isothermal Joule-Thomson coefficient is

$$\left(\frac{\partial H_m}{\partial p} \right)_T = -\mu C_{p,m} = -(1.11 \text{ K atm}^{-1}) \times (37.11 \text{ J K}^{-1} \text{ mol}^{-1}) = \boxed{-41.2 \text{ J atm}^{-1} \text{ mol}^{-1}}$$

If this coefficient is constant in an isothermal Joule-Thomson experiment, then the heat which must be supplied to maintain constant temperature is ΔH in the following relationship

$$\frac{\Delta H / n}{\Delta p} = -41.2 \text{ J atm}^{-1} \text{ mol}^{-1} \quad \text{so} \quad \Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) n \Delta p$$

$$\Delta H = -(41.2 \text{ J atm}^{-1} \text{ mol}^{-1}) \times (10.0 \text{ mol}) \times (-75 \text{ atm}) = \boxed{30.9 \times 10^3 \text{ J}}$$

2E.2(b) For reversible adiabatic expansion

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{1/c} \quad [2E.2a]$$

$$\text{where } c = \frac{C_{V,m}}{R} = \frac{C_{p,m} - R}{R} = \frac{(37.11 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}} = 3.463;$$

therefore, the final temperature is

$$T_f = (298.15 \text{ K}) \times \left(\frac{500 \times 10^{-3} \text{ dm}^3}{2.00 \text{ dm}^3} \right)^{1/3.463} = \boxed{200 \text{ K}}$$

2E.3(b) In an adiabatic process, the initial and final pressures are related by (eqn. 2E.3)

$$p_f V_f^\gamma = p_i V_i^\gamma \quad \text{where} \quad \gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{C_{p,m}}{C_{p,m} - R} = \frac{20.8 \text{ J K}^{-1} \text{ mol}^{-1}}{(20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1}} = 1.67$$

Find V_i from the perfect gas law:

$$V_i = \frac{nRT_i}{p_i} = \frac{(2.5 \text{ mol}) \times (8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (325 \text{ K})}{240 \times 10^3 \text{ Pa}} = 0.0281 \text{ m}^3$$

$$\text{so } V_f = V_i \left(\frac{p_i}{p_f} \right)^{1/\gamma} = (0.0281 \text{ m}^3) \times \left(\frac{240 \text{ kPa}}{150 \text{ kPa}} \right)^{1/1.67} = \boxed{0.0372 \text{ m}^3}$$

Find the final temperature from the perfect gas law:

$$T_f = \frac{p_f V_f}{nR} = \frac{(150 \times 10^3 \text{ Pa}) \times (0.0372 \text{ m}^3)}{(2.5 \text{ mol}) \times (8.31 \text{ J K}^{-1} \text{ mol}^{-1})} = \boxed{269 \text{ K}}$$

Adiabatic work is (eqn. 2E.1)

$$w = C_v \Delta T = (20.8 - 8.31) \text{ J K}^{-1} \text{ mol}^{-1} \times 2.5 \text{ mol} \times (269 - 325) \text{ K} = \boxed{-1.7 \times 10^3 \text{ J}}$$

Problem

2A.4

$$\begin{aligned} w &= -\int_{V_1}^{V_2} p dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V - nb} + n^2 a \int_{V_1}^{V_2} \frac{dV}{V^2} \\ &= -nRT \ln \left(\frac{V_2 - nb}{V_1 - nb} \right) - n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

By multiplying and dividing the value of each variable by its critical value we obtain

$$w = -nR \times \left(\frac{T}{T_c} \right) T_c \times \ln \left(\frac{\frac{V_2}{V_c} - \frac{nb}{V_c}}{\frac{V_1}{V_c} - \frac{nb}{V_c}} \right) - \left(\frac{n^2 a}{V_c} \right) \times \left(\frac{V_c}{V_2} - \frac{V_c}{V_1} \right)$$

$$T_r = \frac{T}{T_c}, \quad V_r = \frac{V}{V_c}, \quad T_c = \frac{8a}{27Rb}, \quad V_c = 3nb \quad [\text{Table 1C.4}]$$

$$w = -\left(\frac{8na}{27b}\right) \times (T_r) \times \ln\left(\frac{V_{r,2} - \frac{1}{3}}{V_{r,1} - \frac{1}{3}}\right) - \left(\frac{na}{3b}\right) \times \left(\frac{1}{V_{r,2}} - \frac{1}{V_{r,1}}\right)$$

The van der Waals constants can be eliminated by defining $w_r = \frac{3bw}{a}$, then $w = \frac{aw_r}{3b}$ and

$$w_r = -\frac{8}{9}nT_r \ln\left(\frac{V_{r,2} - 1/3}{V_{r,1} - 1/3}\right) - n\left(\frac{1}{V_{r,2}} - \frac{1}{V_{r,1}}\right)$$

Along the critical isotherm, $T_r = 1$, $V_{r,1} = 1$, and $V_{r,2} = x$. Hence

$$\frac{w_r}{n} = -\frac{8}{9} \ln\left(\frac{3x-1}{2}\right) - \frac{1}{x} + 1$$

2B.4

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_v\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_v \quad [\text{Derivatives may be taken in any order.}]$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{for a perfect gas [Section 2D.2(a)]}$$

Hence, $\left(\frac{\partial C_v}{\partial V}\right)_T = 0$

Likewise $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ so $\left(\frac{\partial C_p}{\partial p}\right)_T = \left(\frac{\partial}{\partial p}\left(\frac{\partial H}{\partial T}\right)_p\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial p}\right)_T\right)_p$

$$\left(\frac{\partial H}{\partial p}\right)_T = 0 \quad \text{for a perfect gas.}$$

Hence, $\left(\frac{\partial C_p}{\partial p}\right)_T = 0$.

$$2C.6 \quad (a) \quad \Delta_r H^\ominus = \Delta_f H^\ominus(\text{SiH}_2) + \Delta_f H^\ominus(\text{H}_2) - \Delta_f H^\ominus(\text{SiH}_4) \\ = (274 + 0 - 34.3) \text{ kJ mol}^{-1} = \boxed{240 \text{ kJ mol}^{-1}}$$

$$(b) \quad \Delta_r H^\ominus = \Delta_f H^\ominus(\text{SiH}_2) + \Delta_f H^\ominus(\text{SiH}_4) - \Delta_f H^\ominus(\text{Si}_2\text{H}_6) \\ = (274 + 34.3 - 80.3) \text{ kJ mol}^{-1} = \boxed{228 \text{ kJ mol}^{-1}}$$

$$2D.4 \quad (a) \quad V = V(p, T); \text{ hence, } dV = \boxed{\left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT}$$

$$\text{Likewise } p = p(V, T), \text{ so } dp = \boxed{\left(\frac{\partial p}{\partial V}\right)_T dV + \left(\frac{\partial p}{\partial T}\right)_V dT}$$

$$(b) \quad \text{We use } \alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p \text{ [2D.6] and } \kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T \text{ [2D.7] and obtain}$$

$$d \ln V = \frac{1}{V} dV = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_p dT = \boxed{-\kappa_T dp + \alpha dT}.$$

$$\text{Likewise} \quad d \ln p = \frac{dp}{p} = \frac{1}{p}\left(\frac{\partial p}{\partial V}\right)_T dV + \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V dT$$

We express $\left(\frac{\partial p}{\partial V}\right)_T$ in terms of κ_T :

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\left[V\left(\frac{\partial p}{\partial V}\right)_T\right]^{-1} \quad \text{so} \quad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{1}{\kappa_T V}$$

We express $\left(\frac{\partial p}{\partial T}\right)_V$ in terms of κ_T and α

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1 \quad \text{so} \quad \left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V / \partial T)_p}{(\partial V / \partial p)_T} = \frac{\alpha}{\kappa_T}$$

$$\text{so} \quad d \ln p = -\frac{dV}{p\kappa_T V} + \frac{\alpha dT}{p\kappa_T} = \boxed{\frac{1}{p\kappa_T} \left(\alpha dT - \frac{dV}{V}\right)}$$