12. (1). $dU = TdS - pdV$

$$\rightarrow \left(\frac{\partial U}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p$$

$$= C_p - \alpha pV$$

$$\rightarrow \left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + pV\kappa = -T\alpha V + pV\kappa$$

$$C_p = C_V + \frac{\alpha^2 TV}{\kappa}$$

$$\rightarrow \left(\frac{\partial U}{\partial p}\right)_T = -(C_p - C_V)\frac{\kappa}{\alpha} + \kappa pV$$ 得证.

2). $dU = TdS - pdV$.

$$\left(\frac{\partial U}{\partial p}\right)_V = T\left(\frac{\partial S}{\partial p}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial p}\right)_V = T \cdot \frac{C_V}{T}\left(\frac{\partial T}{\partial p}\right)_V = \frac{C_V}{\alpha}.$$

$$\left(\frac{\partial U}{\partial V}\right)_p = T\left(\frac{\partial S}{\partial V}\right)_p - p = T\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial T}{\partial V}\right)_p - p = T \cdot \frac{C_p}{T}\left(\frac{\partial T}{\partial V}\right)_p - p = \frac{C_p}{\partial V} - p.$$

15.

可逆绝热： $dS=0.$

$$dS=\left(\frac{\partial S}{\partial T}\right)_p dT+\left(\frac{\partial S}{\partial p}\right)_T dp.$$

$$\left(\frac{\partial T}{\partial p}\right)_s=-\frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_p}=\frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p}.$$

节流： $dH=0.$

$$dH=\left(\frac{\partial H}{\partial T}\right)_p dT+\left(\frac{\partial H}{\partial p}\right)_T dp.$$

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

$$\Rightarrow\left(\frac{\partial T}{\partial p}\right)_s>\left(\frac{\partial T}{\partial p}\right)_H.$$

19.

(1) $dF = -SdT + dW$

等温：$dF = dW = k(T)x$

$$F = \frac{1}{2}k(T)x^2 + F(T,0)$$

(2) $$S = -\left(\frac{\partial F}{\partial T}\right)_x = -\frac{1}{2}\frac{dk}{dT}x^2 + S(T,0)$$

(3). $$U = F + TS = \frac{1}{2}k(T)x^2 - \frac{1}{2}T\frac{dk}{dT}x^2 + U(T,0)$$

$$= \frac{1}{2}\left(k - T\frac{dk}{dT}\right)x^2 + U(T,0).$$

22.

(1) $S = \frac{4}{3} a T^3 V.$

$Q = T\Delta S = \frac{4}{3} a T^3 \Delta V = \frac{4}{3} a T^3 (V_2 - V_1)$

(2). $Q = 0.$

$dU = Tds - pdV = W = -pdV \rightarrow Tds = 0$

$Tds = 4aT^3VdT + \frac{4}{3}aT^4dV = 0$

$\rightarrow 3VdT + TdV = 0 \rightarrow T^3V = C.$

(3). $Q_1 = T_1(S_2 - S_1)$

$Q_2 = T_2(S_2 - S_1)$

$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}.$

11. $dU = c\,dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]dV.$

$$T\left(\frac{\partial p}{\partial T}\right)_V = T\cdot\left(-\frac{a}{b}\right)$$

$$dU = c\,dT + \left(-\frac{a}{b}T - p\right)dV$$

$$U = \int_{T_0}^{T} c\,dT - \int_{V_0}^{V}\left(\frac{a}{b}T + p\right)dV = cT - \int\left(\frac{V_m}{b} - \frac{V_0}{b}\right)dV$$

$$= cT - \frac{V^2}{2b} + \frac{V_0}{b}V + U_0$$

$$U = cT - \frac{V^2}{2b} + \frac{V_0}{b}V + U_0$$

20. (1).

$$\frac{\partial^2 V}{\partial p \partial T} = -\frac{R}{p^2} = \frac{\partial^2 V}{\partial T \partial p} = -f(p)$$

$$\rightarrow f(p) = \frac{R}{p^2}.$$

(2). $$\int dV = \int \left(\frac{R}{p} + \frac{a}{T^2}\right) dT$$

$$V = \frac{R}{p}T - \frac{a}{T} \rightarrow pV = RT - \frac{ap}{T}$$ 得证.

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p . \quad \frac{\partial C_p}{\partial p} = T\frac{\partial^2 S}{\partial p \partial T} = T\frac{\partial^2 S}{\partial T \partial p} = -T\frac{\partial^2 V}{\partial T^2}$$

$$\frac{\partial C_p}{\partial p} = T \cdot \frac{2a}{T^3} = \frac{2a}{T^2} \rightarrow C_p = \frac{5}{2}R + \frac{2a}{T^2}p.$$