3.解：$p(V-b)=RT$

全微分，得

$$(V-b)\,dp+p\,dV=R\,dT$$

又 $U_m=C_{V,m}T+U_0$

$$dU_m=dW+dQ$$

$$C_{V,m}\,dT=-p\,dV$$

$$\left(\begin{array}{c} C_{p,m}-C_{V,m}=R \\ \dfrac{C_{p,m}-C_{V,m}}{C_{V,m}} \end{array}\right)$$

故而有 $(V-b)\,dp=-p\left(\frac{R}{C_{V,m}}+1\right)dV$

$$\frac{1}{p}\,dp=-\frac{C_{p,m}}{C_{V,m}}\,\frac{1}{V-b}\,dV$$

积分，得

$$\ln p=\ln(V-b)^{-\gamma}+C$$

$$\ln p(V-b)^{\gamma}=C$$

即 $p(V-b)^{\gamma}=\text{const}$

4. (1) 摩尔焓的表达式为

$$H=cT-apT-\frac{1}{2}bp^2$$

(2) $$C_{p,m}=\frac{\partial u}{\partial T}=c-ap$$

$$u=u_0+cT-a\left(\frac{V-V_0-aT}{b}\right)T-\frac{1}{2}b\left(\frac{V-V_0-aT}{b}\right)^2$$

$$C_{V,m}=\frac{\partial u}{\partial T}=c+\frac{a^2}{b}T$$

(3) 不是完全独立的，因为它们共享了系数

6\. 绝热膨胀时，有

$$p_1^{\gamma-1} T_0^{-\gamma} = p_0^{\gamma-1} T_1^{-\gamma}$$

之后，等容降温，有

$$\frac{p_0}{p_2} = \frac{T_1}{T_0}$$

得 $$\left(\frac{p_1}{p_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{-\gamma} = \left(\frac{p_0}{p_2}\right)^{-\gamma}$$

$$(\gamma-1)\ln\frac{p_1}{p_0} + \gamma\ln\frac{p_0}{p_2} = 0$$

$$\gamma = \frac{\ln\frac{p_1}{p_0}}{\ln\frac{p_1}{p_0} + \ln\frac{p_0}{p_2}} = \frac{\ln\frac{p_1}{p_0}}{\ln\frac{p_1}{p_2}}$$