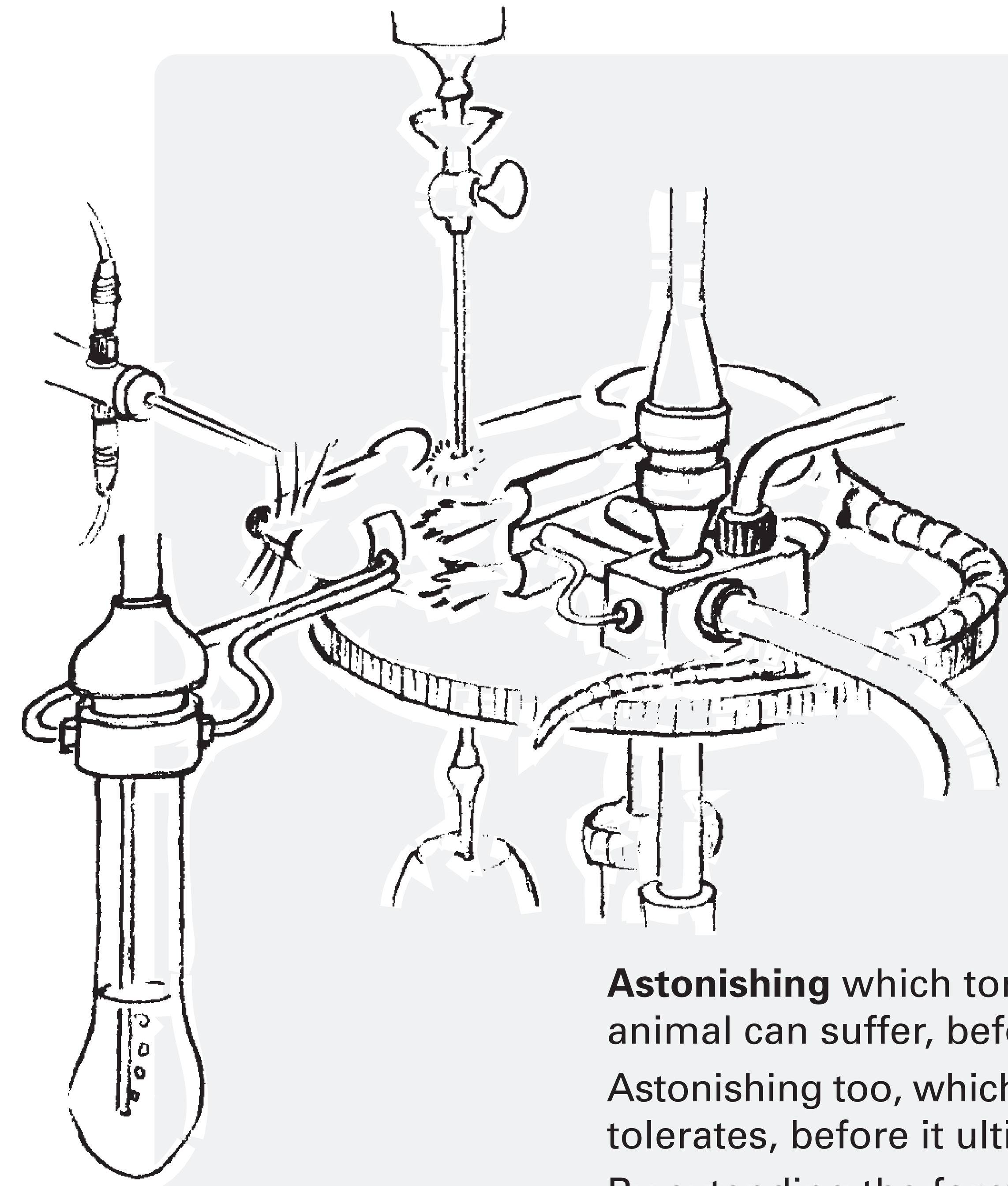
THE EFFICIENCY OF CLASSICAL THERMODYNAMICS

Quantity of Signs used

800 – 700 – 600 – 500 – 400 – 300 – 200 – 100

The calculation effort of five different calculation methods is compared for two examples, arranged by increasing of means. The calculations are as far as possible shown with the same degree of comprehensiveness each starting at a comparable level and ending at the identical or similar equation:

1. following a concept, based on a skillfully developed conception with entropy in the role of heat, predeterminating largely the result;
2. following the same concept, the intermediate calculations, however, restricted to formal operations only;
3. following the classical thermodynamic concept, using an algorithm optimized for this purpose;
4. following the classical thermodynamic concept, the calculation, however, restricted on skillfull application of usual methods;
5. following a typical textbook, assembling all necessary equations, which are often scattered over many paragraphs and cited only by reference.



Astonishing which tortures an experimental animal can suffer, before it will die.

Astonishing too, which manipulations a theory tolerates, before it ultimately fails.

By extending the formalism even severedeficiencies can be successfully compensated.

1st Example:

Difference of the Heats of Reaction

under constant pressure and under constant volume

1

$$\Delta S-\Delta S^{\bullet}=-\Delta S_{\text{Kompr.}}$$
$$=V\gamma\frac{\Delta V}{V\chi}\qquad=\frac{\gamma}{\chi}\Delta V$$

2

$$\Delta S-\Delta S^{\bullet}=\left(\frac{dS}{d\xi}\right)_{Tp}-\left(\frac{dS}{d\xi}\right)_{TV}$$
$$=-\left(\frac{dS}{dp}\right)_{T\xi}\cdot\left(\frac{dp}{d\xi}\right)_{TV}$$
$$=-\left(\frac{dV}{dT}\right)_{p\xi}\cdot\left(\frac{dV}{d\xi}\right)_{Tp}\Big/\left(\frac{dV}{dp}\right)_{T\xi}$$
$$=\frac{\gamma}{\chi}\Delta V$$

3

$$\Delta H-\Delta U^{\bullet}=\left(\frac{dH}{d\xi}\right)_{Tp}-\left(\frac{dU}{d\xi}\right)_{TV}$$
$$=\left(\frac{TdS+Vdp-\mathsf{A}d\xi}{d\xi}\right)_{Tp}-\left(\frac{TdS-pdV-\mathsf{A}d\xi}{d\xi}\right)_{TV}$$
$$=\left[T\left(\frac{dS}{d\xi}\right)_{Tp}-\mathsf{A}\right]-\left[T\left(\frac{dS}{d\xi}\right)_{TV}-\mathsf{A}\right]$$
$$=-T\left(\frac{dS}{dp}\right)_{T\xi}\cdot\left(\frac{dp}{d\xi}\right)_{TV}$$
$$=-T\left(\frac{dV}{dT}\right)_{p\xi}\cdot\left(\frac{dV}{d\xi}\right)_{Tp}\Big/\left(\frac{dV}{dp}\right)_{T\xi}$$
$$=T\frac{\gamma}{\chi}\Delta V$$

4

$$\Delta H-\Delta U^{\bullet}=\left(\frac{dH}{d\xi}\right)_{Tp}-\left(\frac{dU}{d\xi}\right)_{TV}$$
$$=\left(\frac{TdS+Vdp-\mathsf{A}d\xi}{d\xi}\right)_{Tp}-\left(\frac{TdS-pdV-\mathsf{A}d\xi}{d\xi}\right)_{TV}$$
$$=\left[T\left(\frac{dS}{d\xi}\right)_{Tp}-\mathsf{A}\right]-\left[T\left(\frac{dS}{d\xi}\right)_{TV}-\mathsf{A}\right]$$
$$=T\left[\left(\frac{dS}{d\xi}\right)_{Tp}-\left(\frac{dS}{d\xi}\right)_{TV}\right]$$
$$(dS)_T=\left(\frac{dS}{dp}\right)_{T\xi}dp+\left(\frac{dS}{d\xi}\right)_{Tp}d\xi$$
$$(dV)_T=\left(\frac{dV}{dp}\right)_{T\xi}dp+\left(\frac{dV}{d\xi}\right)_{Tp}d\xi=0$$
$$dp=-\left(\frac{dV}{d\xi}\right)_{Tp}d\xi\Big/\left(\frac{dV}{dp}\right)_{T\xi}$$
$$\left(\frac{dS}{d\xi}\right)_{TV}=-\frac{\left(\frac{dS}{dp}\right)_{T\xi}\left(\frac{dV}{d\xi}\right)_{Tp}}{\left(\frac{dV}{dp}\right)_{T\xi}}+\left(\frac{dS}{d\xi}\right)_{Tp}$$
$$\Delta H-\Delta U^{\bullet}=T\cdot\frac{\left(\frac{dS}{dp}\right)_{T\xi}\cdot\left(\frac{dV}{d\xi}\right)_{Tp}}{\left(\frac{dV}{dp}\right)_{T\xi}}$$
$$dG=-SdT+Vdp-\mathsf{A}d\xi$$
$$-\left(\frac{dS}{dp}\right)_{T\xi}=\left(\frac{\partial^2G}{\partial p\partial T}\right)_{\xi}=\left(\frac{\partial^2G}{\partial T\partial p}\right)_{\xi}=\left(\frac{dV}{dT}\right)_{p\xi}$$
$$\Delta H-\Delta U^{\bullet}=T\frac{\gamma}{\chi}\Delta V$$

5

$$\Delta H=\left(\frac{\partial H}{\partial\lambda}\right)_{pT}$$
$$=\left(\frac{\partial(U+pV)}{\partial\lambda}\right)_{pT}$$
$$=\left(\frac{\partial U}{\partial\lambda}\right)_{pT}+p\left(\frac{\partial V}{\partial\lambda}\right)_{pT}$$
$$dU=\left(\frac{\partial U}{\partial\lambda}\right)_{VT}d\lambda+\left(\frac{\partial U}{\partial V}\right)_{\lambda T}dV$$
$$dV=\left(\frac{\partial V}{\partial\lambda}\right)_{pT}d\lambda$$
$$dU=\left[\left(\frac{\partial U}{\partial\lambda}\right)_{VT}+\left(\frac{\partial U}{\partial V}\right)_{\lambda T}\left(\frac{\partial V}{\partial\lambda}\right)_{pT}\right]d\lambda$$
$$\left(\frac{\partial U}{\partial\lambda}\right)_{pT}=\left(\frac{\partial U}{\partial\lambda}\right)_{VT}+\left(\frac{\partial U}{\partial V}\right)_{\lambda T}\left(\frac{\partial V}{\partial\lambda}\right)_{pT}$$
$$\left(\frac{\partial H}{\partial\lambda}\right)_{pT}=\left(\frac{\partial U}{\partial\lambda}\right)_{VT}+\left[\left(\frac{\partial U}{\partial V}\right)_{\lambda T}+p\right]\left(\frac{\partial V}{\partial\lambda}\right)_{pT}$$
$$\Delta H-\Delta U^{\bullet}=\left[\left(\frac{\partial U}{\partial V}\right)_{\lambda T}+p\right]\Delta V$$
$$dS=\frac{dQ_{\text{rev}}}{T}$$
$$=\left(\frac{\partial S}{\partial V}\right)_{T\lambda}dV+\left(\frac{\partial S}{\partial T}\right)_{V\lambda}dT$$
$$dU=\delta Q+\delta A=\delta Q-pdV$$
$$=\left(\frac{\partial U}{\partial T}\right)_{V\lambda}dT+\left(\frac{\partial U}{\partial V}\right)_{T\lambda}dV$$
$$dQ=dU+p\,dV$$
$$=\left(\frac{\partial U}{\partial T}\right)_{V\lambda}dT+\left[\left(\frac{\partial U}{\partial V}\right)_{T\lambda}+p\right]dV$$
$$dS=\frac{dQ_{\text{rev}}}{T}$$
$$=\frac{dU+pdV}{T}$$
$$=\frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_{V\lambda}dT+\left(\frac{\partial U}{\partial V}\right)_{T\lambda}dV+p\,dV\right]$$
$$dS=\frac{C_V dT}{T}+\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T\lambda}+p\right]dV$$
$$\left(\frac{\partial S}{\partial T}\right)_{V\lambda}=\frac{C_V}{T}$$
$$\left(\frac{\partial S}{\partial V}\right)_{T\lambda}=\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T\lambda}+p\right]$$
$$\left(\frac{\partial^2S}{\partial T\partial V}\right)_{\lambda}=\left(\frac{\partial^2S}{\partial V\partial T}\right)_{\lambda}$$
$$\frac{1}{T}\left(\frac{\partial C_V}{\partial V}\right)_{T\lambda}=\frac{1}{T}\left(\frac{\partial^2U}{\partial V\partial T}\right)_{\lambda}+\frac{1}{T}\left(\frac{\partial p}{\partial T}\right)_{V\lambda}-\frac{1}{T^2}\left[\left(\frac{\partial U}{\partial V}\right)_{T\lambda}+p\right]$$
$$\left(\frac{\partial^2U}{\partial V\partial T}\right)_{\lambda}=\left(\frac{\partial C_V}{\partial V}\right)_{T\lambda}$$
$$\left(\frac{\partial U}{\partial V}\right)_{T\lambda}=T\left(\frac{\partial p}{\partial T}\right)_{V\lambda}-p$$
$$\left(\frac{\partial p}{\partial T}\right)_{V\lambda}=-\frac{\left(\frac{\partial V}{\partial p}\right)_{p\lambda}}{\left(\frac{\partial V}{\partial p}\right)_{T\lambda}}=\frac{\gamma}{\chi}$$
$$\left(\frac{\partial U}{\partial V}\right)_{T\lambda}=T\frac{\gamma}{\chi}-p$$
$$\Delta H-\Delta U^{\bullet}=T\frac{\gamma}{\chi}\Delta V$$

2nd Example:

Temperature Coefficient of the Heat Evaporation

1

$$\left(\frac{dp}{dT}\right)_{\mathsf{A}\xi}=\left(\frac{dp}{dT}\right)_V=\left(\frac{dS}{dV}\right)_T$$
$$=\Delta S/\Delta V$$
$$\left(\frac{d\Delta S}{dT}\right)_{\mathsf{A}\xi}=\Delta\hat{C}-\Delta(V\gamma)\cdot\frac{\Delta S}{\Delta V}$$

2

$$\left(\frac{d\Delta S}{dT}\right)_{\mathsf{A}\xi}=\left(\frac{d\Delta S}{dT}\right)_{p\xi}+\left(\frac{d\Delta S}{dp}\right)_{T\xi}\left(\frac{dp}{dT}\right)_{\mathsf{A}\xi}$$
$$=\Delta\left(\frac{dS}{dT}\right)_{p\xi}+\Delta\left(\frac{dS}{dp}\right)_{T\xi}\left(\frac{dS}{dV}\right)_{pT}$$
$$=\Delta\hat{C}-\Delta\left(\frac{dV}{dT}\right)_{p\xi}\frac{\left(\frac{dS}{d\xi}\right)_{pT}}{\left(\frac{dV}{d\xi}\right)_{pT}}$$
$$=\Delta\hat{C}-\Delta S\cdot\frac{\Delta(V\gamma)}{\Delta V}$$

3

$$\left(\frac{d\Delta H}{dT}\right)_{\mathsf{A}\xi}=\left(\frac{d\Delta H}{dT}\right)_{p\xi}+\left(\frac{d\Delta H}{dp}\right)_{T\xi}\left(\frac{dp}{dT}\right)_{\mathsf{A}\xi}$$
$$=\Delta\left(\frac{dH}{dT}\right)_{p\xi}+\Delta\left(\frac{dH}{dp}\right)_{T\xi}\left(\frac{dS}{dV}\right)_{pT}$$
$$=\Delta C_p+\Delta\left(\frac{Vdp+TdS-\mathsf{A}d\xi}{dp}\right)_{T\xi}\left(\frac{dS}{d\xi}\right)_{pT}\Big/\left(\frac{dV}{d\xi}\right)_{pT}$$
$$=\Delta C_p+\Delta\left[V+T\left(\frac{dS}{dp}\right)_{T\xi}\right]\frac{\Delta S}{\Delta V}$$
$$=\Delta C_p+\left[\Delta V-T\Delta\left(\frac{dV}{dT}\right)_{p\xi}\right]\frac{\Delta S}{\Delta V}$$
$$=\Delta C_p+\Delta S-T\Delta S\,\frac{\Delta(V\gamma)}{\Delta V}$$
$$\Delta H=\Delta\left(\frac{dH}{d\xi}\right)_{pT}$$
$$=\left(\frac{Vdp+TdS-\mathsf{A}d\xi}{d\xi}\right)_{pT}$$
$$=T\left(\frac{dS}{d\xi}\right)_{pT}$$
$$=T\Delta S$$
$$\left(\frac{d\Delta H}{dT}\right)_{\mathsf{A}\xi}=\Delta C_p+\frac{\Delta H}{T}-\Delta H\frac{\Delta(V\gamma)}{\Delta V}$$

4

$$\left(\frac{d\Delta H}{dT}\right)_{\text{koex}}$$
$$\Delta G=0$$
$$d(\Delta G)=0$$
$$dH_i=TdS_i+V_idp$$
$$dG_i=-S_idT+V_idp$$
$$G_i=H_i-TS_i$$
$$dS_i=\left(\frac{dS_i}{dT}\right)_p dT+\left(\frac{dS_i}{dp}\right)_T dp$$
$$\Delta G=\Delta H-T\Delta S=0$$
$$\Delta S=\frac{\Delta H}{T}$$
$$d(\Delta G)=\Delta(dG)$$
$$=-\Delta SdT+\Delta Vdp=0$$
$$dp=\frac{\Delta H}{T\Delta V}dT$$
$$-\left(\frac{dS_i}{dp}\right)_T=\frac{\partial^2G_i}{\partial p\partial T}$$
$$=\frac{\partial^2G_i}{\partial T\partial p}=\left(\frac{dV_i}{dT}\right)_p=V_i\gamma_i$$
$$C_{pi}=\left(\frac{dH_i}{dT}\right)_p=\left(\frac{T\,dS_i+V_idp}{dT}\right)_p$$
$$=T\left(\frac{dS_i}{dT}\right)_p$$
$$dS_i=\frac{C_{pi}}{T}dT-V_i\gamma_idp$$
$$dH_i=C_{pi}dT+\left[V_i-TV_i\gamma_i\right]dp$$
$$\Delta(dH)=\Delta C_pdT+\left[\Delta V-T\Delta(V\gamma)\right]dp$$
$$d(\Delta H)=\left[\Delta C_p+\left[\Delta V-T\Delta(V\gamma)\right]\frac{\Delta H}{T\Delta V}\right]dT$$
$$\left(\frac{d\Delta H}{dT}\right)_{\text{koex}}=\Delta C_p+\frac{\Delta H}{T}-\Delta H\frac{\Delta(V\gamma)}{\Delta V}$$

5

$$dH=\delta Q+Vdp$$
$$=\left(\frac{\partial H}{\partial T}\right)_{pn}dT+\left(\frac{\partial H}{\partial p}\right)_{Tn}dp+\left(\frac{\partial H}{\partial n}\right)_{pT}dn$$
$$\left(\frac{\partial H}{\partial n}\right)_{pT}=\frac{dQ}{dn}\equiv L_p$$
$$H_D-H_{fl}$$
$$dS=\frac{dH-Vdp}{T}$$
$$=\left(\frac{\partial S}{\partial T}\right)_{pn}dT+\left(\frac{\partial S}{\partial p}\right)_{Tn}dp+\left(\frac{\partial S}{\partial n}\right)_{pT}dn$$
$$\frac{dH}{T}=\left(\frac{\partial S}{\partial n}\right)dn$$
$$\left(\frac{\partial S}{\partial n}\right)_{pT}=\frac{1}{T}\left(\frac{\partial H}{\partial n}\right)_{pT}=\frac{L_p}{T}$$
$$S_D-S_{fl}$$
$$dL_p=\left(\frac{\partial L_p}{\partial T}\right)_p dT+\left(\frac{\partial L_p}{\partial p}\right)_T dp$$
$$dS=\frac{dQ_{\text{rev}}}{T}$$
$$=\left(\frac{\partial S}{\partial p}\right)_T dp+\left(\frac{\partial S}{\partial T}\right)_p dT$$
$$dH=\delta Q+Vdp$$
$$=\left(\frac{\partial H}{\partial T}\right)_p dT+\left(\frac{\partial H}{\partial p}\right)_T dp$$
$$\delta Q=dH-Vdp$$
$$=\left(\frac{\partial H}{\partial T}\right)_p dT+\left[\left(\frac{\partial H}{\partial p}\right)_T-V\right]dp$$
$$dS=\frac{dQ_{\text{rev}}}{T}=\frac{dH-Vdp}{T}$$
$$=\frac{1}{T}\left[\left(\frac{\partial H}{\partial T}\right)_p dT+\left(\frac{\partial H}{\partial p}\right)_T dp-Vdp\right]$$
$$dS=\frac{C_pdT}{T}+\frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T-V\right]dp$$
$$\left(\frac{\partial S}{\partial T}\right)_p=\frac{C_p}{T}$$
$$\left(\frac{\partial S}{\partial p}\right)_T=\frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T-V\right]$$
$$\frac{\partial^2S}{\partial T\partial p}=\frac{\partial^2S}{\partial p\partial T}$$
$$\frac{1}{T}\left(\frac{\partial C_p}{\partial p}\right)_T=\frac{1}{T}\frac{\partial^2H}{\partial p\partial T}-\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p-\frac{1}{T^2}\left[\left(\frac{\partial H}{\partial p}\right)_T-V\right]$$
$$\left(\frac{\partial H}{\partial T}\right)_p=C_p$$
$$\frac{\partial^2H}{\partial p\partial T}=\left(\frac{\partial C_p}{\partial p}\right)_T$$
$$\left(\frac{\partial H}{\partial p}\right)_T=V-T\left(\frac{\partial V}{\partial T}\right)_p$$
$$dL_p=\left(C_{p,D}-C_{p,fl}\right)dT+\left[V_D-T\left(\frac{\partial V_D}{\partial T}\right)_p-V_{fl}+T\left(\frac{\partial V_{fl}}{\partial T}\right)_p\right]dp$$
$$=\Delta C_pdT+\left[\Delta V-T\left(\frac{\partial\Delta V}{\partial T}\right)_p\right]dp$$
$$\left(\frac{dL_p}{dT}\right)_{\text{koex}}=\Delta C_p+\left[\Delta V-T\left(\frac{\partial\Delta V}{\partial T}\right)_p\right]\frac{dp_s}{dT}$$
$$\mu_D=\mu_{fl}$$
$$d\mu_D=d\mu_{fl}$$
$$d\mu=\left(\frac{\partial\mu}{\partial p}\right)_T dp+\left(\frac{\partial\mu}{\partial T}\right)_p dT$$
$$dG=-SdT+Vdp+\mu dn$$
$$\frac{\partial^2G}{\partial n\partial T}=\frac{\partial^2G}{\partial T\partial n}$$
$$\frac{\partial^2G}{\partial n\partial p}=\frac{\partial^2G}{\partial p\partial n}$$
$$\left(\frac{\partial\mu_i}{\partial T}\right)_{pn_i}=-S_i$$
$$\left(\frac{\partial\mu_i}{\partial p}\right)_{Tn_i}=V_i$$
$$d\mu_D=V_D\,d\,p_s-S_D\,dT$$
$$=d\mu_{fl}=V_{fl}\,d\,p_s-S_{fl}\,dT$$
$$\left(\frac{dp_s}{dT}\right)_{\text{koex}}=\frac{S_D-S_{fl}}{V_D-V_{fl}}$$
$$\left(\frac{dp_s}{dT}\right)_{\text{koex}}=\frac{L_p}{T\cdot(V_D-V_{fl})}$$
$$\left(\frac{dL_p}{dT}\right)_{\text{koex}}=\Delta C_p+\frac{L_p}{T}-L_p\left(\frac{\partial\ln\Delta V}{\partial T}\right)_p\frac{\Delta(V\gamma)}{\Delta V}$$

Degree of Restriction

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